

AD-778 825

ADVANCED LITHIUM-WATER BATTERY FOR
ELECTRONIC COUNTERMEASURE DEVICES

Hubert F. Bauman

Lockheed Missiles and Space Company,
Incorporated

Prepared for:

Air Force Systems Command

26 November 1973

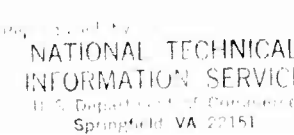
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFAPL-TR-73-120	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD-778 825
4. TITLE (and Subtitle) ADVANCE LITHIUM-WATER BATTERY FOR ELECTRONIC COUNTERMEASURE DEVICES		5. TYPE OF REPORT & PERIOD COVERED Report 1 Nov 1972 - 1 Nov 1973
		6. PERFORMING ORG. REPORT NUMBER LMSC-D356295
7. AUTHOR(s) Hubert F. Bauman		8. CONTRACT OR GRANT NUMBER(s) F33615-73-C-2021
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lockheed Missiles & Space Co., Inc. 3251 Hanover St., Palo Alto, Ca. 94304		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Systems Command United States Air Force		12. REPORT DATE 26 November 1973
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 57
		15. SECURITY CLASS. (of this report) Unclassified
15a. DECLASSIFICATION DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Distribution of this document is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Lithium-Water Battery Lithium Anode Electrochemical Characterization Energy Conversion		
<div style="text-align: center;">  <p>NATIONAL TECHNICAL INFORMATION SERVICE U. S. Department of Commerce Springfield, VA 22151</p> </div>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The lithium-water cell was characterized during the present study and marked improvements made in lithium utilization efficiency by the selection of electrolyte and in the cell potential by the use of catalyzed cathodes. Cell studies show that a spaced electrode cell can be operated with lithium hydroxide concentrations of 2.5- to 3.5-M in the electrolyte at 10° to 30°C at current densities to 1.5 A/in. ² . About double this power density is expected with optimized cell construction. Selected electrolytes may be used that allow 50 to 80% lithium-utilization efficiency		

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at potentials of over 1 V at temperatures to 30°C. Catalyzed cathodes have reduced polarization and their use will increase by 10 to 25% the power capability of the system.

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AIR FORCE/56780/18 April 1971/200

PREFACE

This Technical Progress Report describes the work performed on the Advanced Lithium-Water Battery For Electronic Countermeasures Devices program during the period 11 November 1972 through 1 November 1973. This activity has been conducted by the Lockheed Palo Alto Research Laboratory for the United States Air Force, Air Force Systems Command, Hq 4950th Test Wing 4950/PMNB, Wright-Patterson AFB, Ohio 45433, under Contract F33615-73-C-2021. The contract monitor is Dr. J. J. Lander, AFAPL/POE.

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Section 1

INTRODUCTION

BACKGROUND

Lockheed Palo Alto Research Laboratory personnel have discovered a method to react alkali metals directly with aqueous electrolytes in an electrochemical cell to produce electrical energy. This reaction is accomplished in a simple cell without the use of separators, barriers, or amalgams to limit the normally rapid reaction rates between the metal and the aqueous electrolyte. An inert but electrically conductive cathode is used in the cell; the anode and an oxidant, usually water, are consumed. Both sodium and lithium have been used as anodes, lithium proving superior to date.

OBJECTIVE

The objective of this effort is to provide advanced battery technology leading to improved primary battery power supplies for Air Force applications. The emphasis is on the establishment of the basic electrochemical performance of the lithium-water battery with increases in Faradaic efficiencies and lithium utilization and with the reduction of voltage losses. The goal of the cell investigation and battery optimization is to establish a basis for engineered prototype batteries yielding energy densities of over 60 Whr/lb and of 12 Whr/in.³ in reference configurations. The requirements encompassing these goals are shown in Table 1.

SCOPE

The exploratory development effort is a 24-month program designed to encompass:

- Experimental studies of anode, cathode, and electrolyte formulations of the basic electrochemical couple
- Definition of processes and components for fabrication of cells and batteries

TABLE 1. BATTERY REQUIREMENTS

Category	Parameter	Requirement												
Electrical	Voltage	28 V nominal with a minimum of 24 V and a maximum of 30 V												
	Current	20 A, resistive load												
	Activation time	1 sec or less when activated by a dc pulse												
	Operating life	45 minutes continuous												
	Electrical noise	Less than 2 V peak to peak												
	Wet stand	15 minutes after activation before the application of the load												
Physical	Volume	35 cu in., maximum												
	Weight	7 lb or less												
Environmental Activation and Operating Conditions	Temperature	+55° to +165° F. In no instance shall the outside skin temperature of the battery exceed 250° F												
	Pressure	Sea level to 0.043 in. of mercury (150,000 ft)												
	Orientation	Activation and operation in all positions												
	Vibration	Random for 2 minutes per axis in each of three mutually perpendicular axes <table><tr><td><u>Spectral Density</u></td><td><u>Frequency Range (Hz/sec)</u></td></tr><tr><td>6 dB/octave rise</td><td>10 to 35</td></tr><tr><td>0.12 g²/Hz</td><td>35 to 335</td></tr><tr><td>12 dB²/octave rise</td><td>335 to 456</td></tr><tr><td>0.4 g²/Hz</td><td>450 to 1500</td></tr><tr><td>6 dB/octave roll-off</td><td>1500 to 2000</td></tr></table>	<u>Spectral Density</u>	<u>Frequency Range (Hz/sec)</u>	6 dB/octave rise	10 to 35	0.12 g ² /Hz	35 to 335	12 dB ² /octave rise	335 to 456	0.4 g ² /Hz	450 to 1500	6 dB/octave roll-off	1500 to 2000
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	12 dB ² /octave rise	335 to 456												
	0.4 g ² /Hz	450 to 1500												
6 dB/octave roll-off	1500 to 2000													
Shock	140 g half-sinewave pulse for 0.75 msec minimum duration along the longitudinal axis													
Acceleration	69 g minimum along and perpendicular to the longitudinal axis													
Spin	11 ± 2 rev/sec in each direction about the longitudinal axis													
Radiation hardening	Desirable													
Environmental Nonoperating Conditions	Temperature	-35° to +150° F												
	Shelf life	Unactivated storage life of 5 years												
	Pressure	Sea level to 3.44 in. of mercury												
	Vibration	Sinusoidal at a sweep rate of 0.5 octave/min from 5 to 300 to 4 Hz/sec <table><tr><td><u>Vibration Double Amplitude of Peak Acceleration</u></td><td><u>Frequency Range (Hz/sec)</u></td></tr><tr><td>0.4 in.</td><td>5 to 16</td></tr><tr><td>5.0 g</td><td>16 to 50</td></tr><tr><td>2.1 g</td><td>50 to 200</td></tr></table>	<u>Vibration Double Amplitude of Peak Acceleration</u>	<u>Frequency Range (Hz/sec)</u>	0.4 in.	5 to 16	5.0 g	16 to 50	2.1 g	50 to 200				
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	0.4 in.	5 to 16												
	5.0 g	16 to 50												
2.1 g	50 to 200													
Shock	100 g, 6 msec terminal peak sawtooth shock pulse as shown in Fig. 316-1, Procedure IV, of MIL-STD-810													
Humidity	0 to 100% relative humidity up to 80° F, and a humidity corresponding to a dew point of 80° F at temperatures above 80° F													

- Experimental validation of design configurations
- Evaluation of breadboard batteries

During the first 12 months, the program will emphasize:

- (1) Establishment of the fundamental performance characteristics of the basic electrochemical couple
- (2) Fundamental investigations of anode and cathode electrodes, and electrolyte formulations, leading to substantial increases in Faradaic efficiencies and lithium utilization, as well as reduction in voltage losses through anode film.

The second 12-month period will emphasize:

- (1) Design, fabrication, and test of cells made with the best combinations of anode, cathode, and electrolyte formulations
- (2) Cell and battery design optimization
- (3) Delivery of breadboard battery units based on optimized configurations of reserve battery design

APPROACH

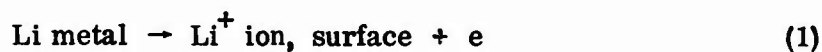
Previous work with the lithium-water cell system at the Palo Alto Research Laboratory has normally used test cells in which the anode and the cathode are in direct contact with each other, a film on the anode serving to prevent direct shorting. This system has allowed the realization of extremely high power and energy densities. In this test system, however, it is difficult to separate the reactions of the anode and the cathode. For this contract, it was decided to use spaced electrodes with a reference electrode to obtain the maximum data during the basic cell characterization and the study of the individual system components, while recognizing that the maximum power obtainable from the lithium-water electro-chemical system would not be obtained. It is to be expected that the space electrode system would indicate parametric trends which would be translatable to other cell configurations.

Similarly, fixed electrodes will be used in the basic characterization cell while it is recognized that a system in which one electrode is allowed to move has advantages in obtaining the highest energy density. The simplicity of the fixed electrode system recommends it for basic studies although moving electrodes may be considered for breadboard batteries if such a system can be made compatible with shock and vibration requirements for a final battery design.

Section 2
THEORY OF THE LITHIUM-WATER POWER CELL

BASIC LITHIUM-WATER CELL REACTIONS

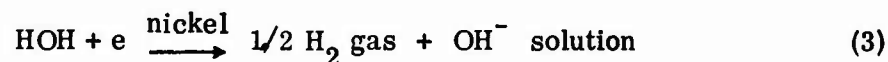
The lithium-water power cell derives electrical energy from the electrochemical reaction of lithium metal with water to produce lithium hydroxide and hydrogen gas. The anodic reaction which occurs at the lithium surface can be written:



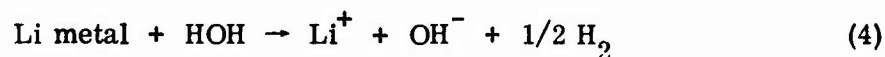
and



The cathodic reaction which occurs at an inert electron conducting surface, e.g., nickel may be written:



Thus, the net reaction for the production of useful electrical energy is written:



The standard potential E° for this cell reaction at 25°C and unit activity of the participating species is 2.217 V from data given by Latimer.* The cell voltage in

*W. M. Latimer, Oxidation Potentials, N.Y., Prentice-Hall, 1949

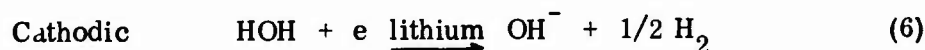
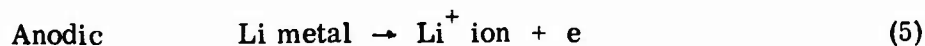
lithium hydroxide solution at 3.0 molal concentration is calculated to be 2.197 V at 25°C from the following equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{LiOH}} a_{\text{H}_2}^{1/2}}{a_{\text{H}_2\text{O}}}$$

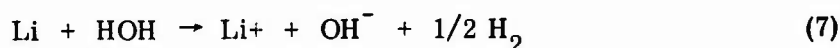
The activities a of the various species were calculated in Robinson and Stokes* which were selected for 3.0 molal lithium hydroxide solutions at 25°C:

- Activity coefficient for LiOH 0.467
- Activity of water approximately 0.90
- Partial pressure of hydrogen 740 mm Hg.

The concentration of 3.0 molal LiOH corresponds to 2.95 molar LiOH solutions, which is a value of concentration for LiOH yielding optimum electrical cell properties. Lithium spontaneously reacts with water, even with the cell on open circuit, by following reactions:



with a net reaction



This net reaction is identical to the reaction for production of useful energy (4), but this reaction (7) is a corrosion reaction producing no useful current. The potential measured at the terminals of the lithium-water cell is less than the theoretical 2.197 V at 3.0 molal LiOH solution at concentration at 25°C because of the mixed potential formed by both reactions at the lithium surface. The commonly measured open-circuit potential is 1.86 V at 3 molar solution of LiOH and 25°C temperature. The rate of reaction (4), the reaction of lithium with water to form useful current, may be determined

*R. A. Robinson and R. H. Stokes, Electrolyte Solutions, London, Butterworth's Science Publications, 1959

by measuring current in amperes produced by the cell in the external circuit. The rate of reaction (7), the spontaneous reaction of lithium with water at the lithium surface, cannot be directly measured but can be estimated by measuring the weight loss of lithium or the volumetric loss of lithium during an experiment at constant current, or by measuring the total hydrogen gassing rate during a cell reaction and calculating the total reaction rate of the lithium. The corrosion reaction rate of lithium reaction (7) can then be calculated as the difference between the total reaction rate determined experimentally and the useful electrical current measure in amperes. The total reaction rate or total current for lithium reaction is calculated from the hydrogen evolution rate by the following equation:

$$I_{\text{total}} = (dV/dt) FP/RT$$

where

- F = the faraday constant
- P = the pressure of hydrogen corrected for water vapor content
- R = the gas constant
- T = the absolute temperature
- (dV/dt) = the hydrogen evolution rate for the cell

The total current is then:

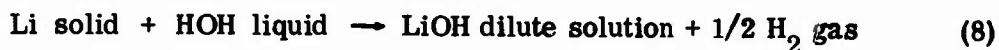
$$I_{\text{total}} = I_{\text{useful}} + I_{\text{corrosion}}$$

and the efficiency of lithium utilization (current efficiency) n is

$$n = I_{\text{useful}}/I_{\text{total}}$$

The useful currents obtained from a lithium-water power cell range to a maximum of 4 A/in.² electrode surface at 1.0 V per cell in 3 molar LiOH electrolyte solution at 35°C. The corrosion currents for these experiments ranged from 6 to 8 A/in.² area, and is dependent on the cell electrolyte concentration, the electrolyte temperature, and the condition of the cathode surface. Thus, current efficiencies from 40 to 30 percent have been obtained under these conditions.

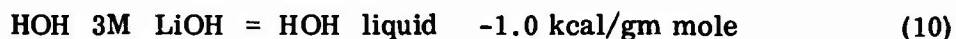
The heat produced by the lithium reaction with water for the reaction:



is estimated from the enthalpy change which is -52.6 kcal/gm mole of reaction for the reactant and product states noted. Estimates of enthalpy changes for the following reactions:



and



yield a heat production of 51.6 kcal/gm mole of reaction as written:



This quantity of heat will be obtained in cells operated at open circuit for the corrosion current. When cells are operated to obtain useful current, the heat produced will be less than the stated value, reduced by the electrical work performed. The cell heat production can be expressed as a function of the useful current I_1 and of the corrosion current I_2 by the following equation:

$$Q/t = [(-\Delta H/F) - V] I_1 + (-\Delta H/F) I_2$$

where

Q = the heat (W-sec)

t = the time (sec)

Q_t = the heat rate

ΔH = the enthalpy change for the reaction of lithium with water for both the useful reaction current I_1 and the corrosion reaction current I_2

F = the faraday constant

V = the cell voltage

I_1 and I_2 = the rates of the reactions expressed in amperes current

If the current efficiency n is expressed:

$$n = \frac{I_1}{I_1 + I_2}.$$

then the equations reduce to the following:

$$Q/I_1 t = (-\Delta H/F) 1/n - V$$

The corrosion current I_2 is dependent on both electrolyte concentration and cell temperature. Heat produced by the cell reaction must be removed continuously to permit steady-state operation for long time periods. In the present experimental conditions, the heat absorption is accomplished by circulation and cooling of cell electrolyte through the cell. This technique minimizes the cell temperature increase and also reduces the cell electrolyte concentration changes during experimental runs. Estimation of the magnitude of cell heat evolution is necessary for design of peripheral cell cooling equipment using either conduction by liquid flow or heat transfer through air from a radiating and convecting surface. Operation of cells at elevated temperatures (higher than ambient) may be possible through the use of lithium alloy anodes which reduce lithium activity or through the use of mixed solvent electrolytes which lower the water activity. Such high temperature operation is advantageous in coping with the problem of heat removal; by maximizing the thermal cell gradient, a high heat removal rate may be obtained.

EXPERIMENTAL APPARATUS

Test Cell

The cell of the basic cell characterization was designed to use a 10 in.² electrode 4 in. wide and 2 1/2 in. high. Fixed electrodes are used in the cell with an initial 0.060-in.

spacing. A reference electrode is connected to the cell through a Luggin capillary adjacent to the cathode. In the past it has been difficult in this laboratory to secure data at elevated temperatures because of the inability to remove heat effectively from the cell. At elevated temperatures, the corrosion rate of the lithium, which is strongly exothermic, increases rapidly with temperature, and control is therefore essential. For this test cell, where high temperature operation is desirable, a hollow anode which could be liquid-cooled was designed. The temperature and flow rate of this conditioning water can then be used to maintain a consistent operating temperature in the cell. Polypropylene was chosen as the material for the cell body because of its resistance to alkaline solution attack as well as its compatibility with organic solvents which might be used as electrolyte additives.

Figure 1 shows an assembly drawing of the test cell. The vertical section shows the plain nickel cathode on the right, the water-cooled anode holder and anode on the left, with an initial 0.065-in. spacing between the electrode faces. The electrolyte enters from the bottom through a slit the full width of the electrodes and is removed from the top through another slit. The central electrolyte exit is made sufficiently large to handle the volume of hydrogen which may be generated in the cell. A thermocouple hole is available in the anode to sense temperature at the electrolyte electrode face during the cell run. A capillary is located adjacent to the cathode for connection to a reference cathode.

Figure 2 shows the cathode in position in the cell body with the anode assembly held in front. The structure above the cell is the gas-liquid separator for removing hydrogen for measurement from the electrolyte as it emerges from the top of the cell.

Test Stand

Cell parameters which must be measured are the current, cell voltage, anode-reference and anode-cathode reference voltage, and total hydrogen evolved from the cell. Two liquid flow loops, the electrolyte and the conditioning water (shown on Figure 3), require a measurement both of inlet and outlet temperature and of flow rate. Most of these

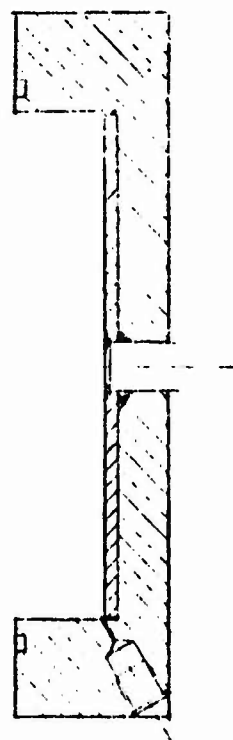
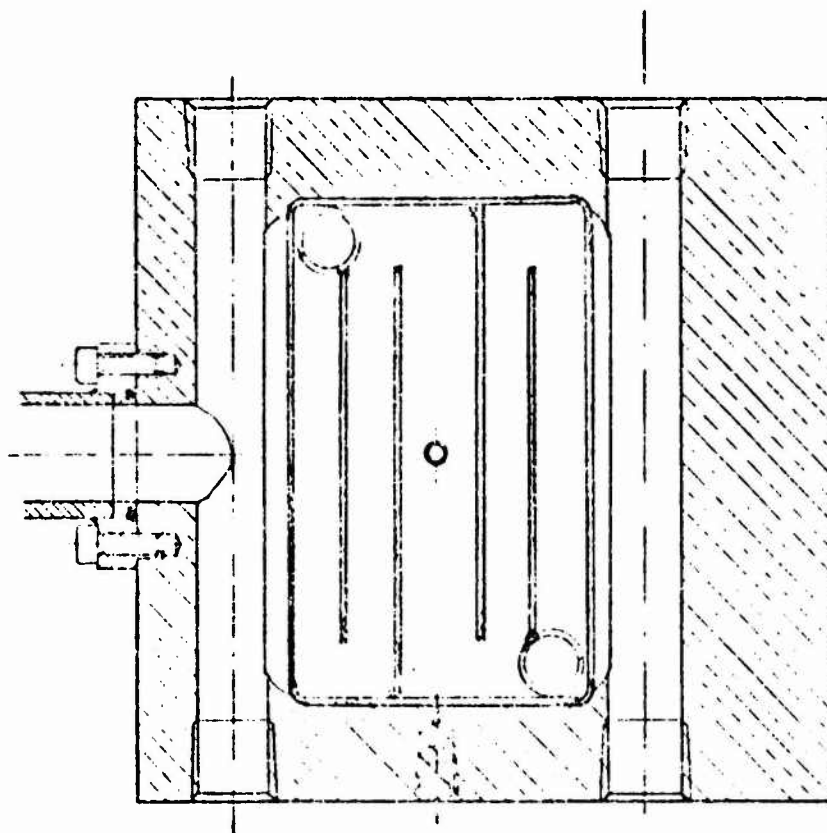
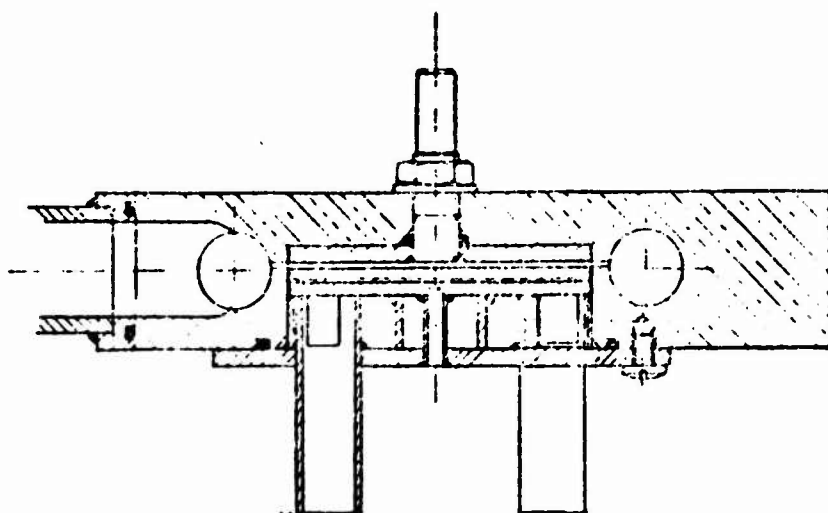


Figure 1. Test Cell

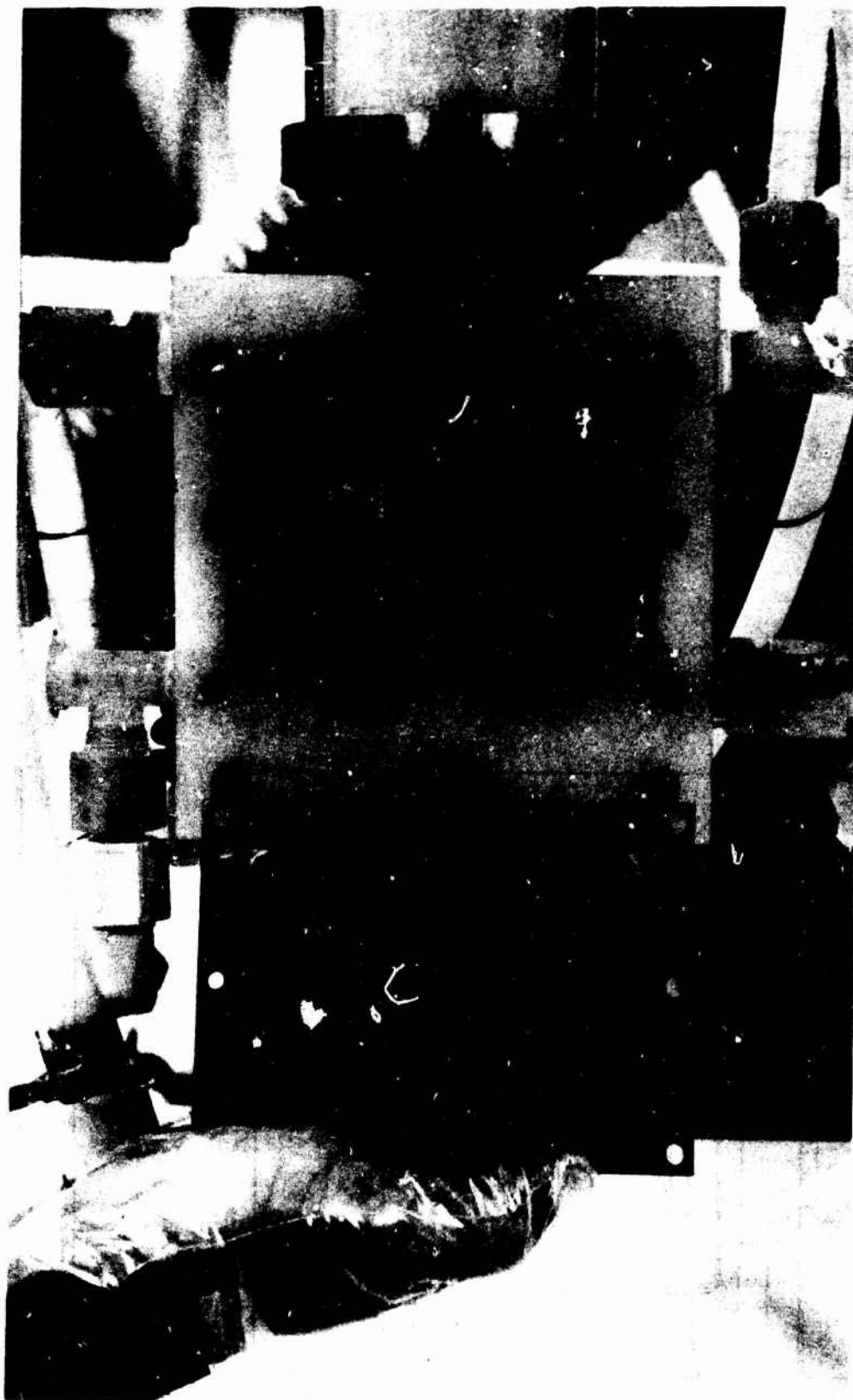


Figure 2. Anode and Cathode With Test Cell

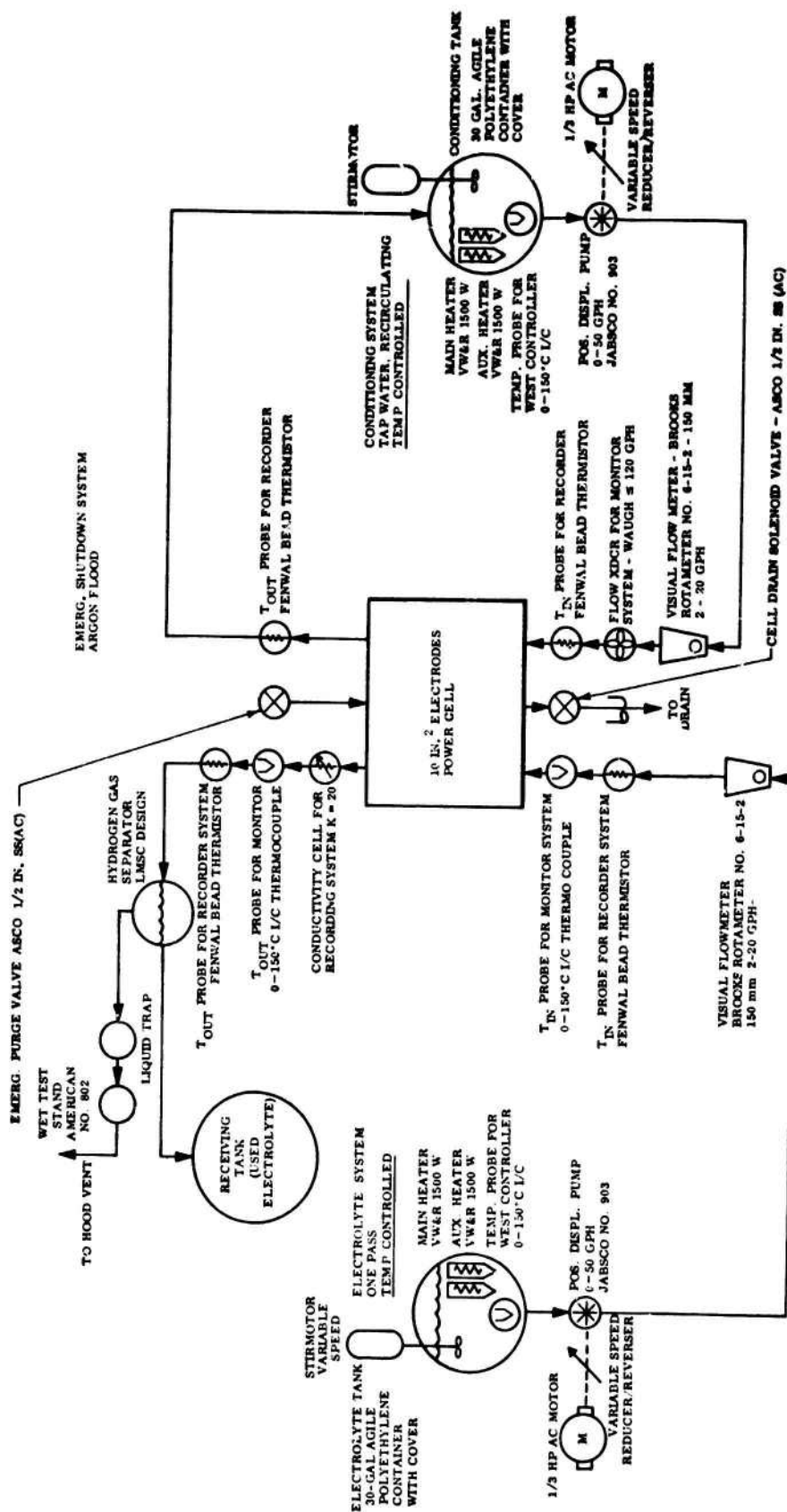


Figure 3. Test Cell Flow Chart

parameters had their values indicated by meters for visual following of the test and a parallel input to the recording system. Voltages and current were measured by conventional meters except for the reference potentials where voltmeters with input impedance in excess of 10^9 ohms were used to prevent loading of the reference electrode.

A Cd/CdO half cell was used initially as the reference electrode. This electrode consisted of a cadmium metal strip imbedded in a plastic plug that screwed into the cell body. The portion of the cadmium strip that was immersed in the electrolyte was cycled anodically and cathodically in LiOH initially to build up a CdO layer. The operation of this reference was generally satisfactory when LiOH electrolytes were used in the cell, but a hydrogen half cell was designed for use in solutions to which other materials were added. The hydrogen reference cell consisted of a plastic block with an electrolyte cavity containing a black platinum-covered screen positioned so as to be covered with electrolyte. An inlet for hydrogen was placed in the bottom of the electrolyte cavity. The reference cell was connected to the test cell with a plastic tube entering the side of the reference cell block and connecting to the test cell through the normal reference electrode inlet. Hydrogen to keep the black platinum electrode activated was obtained from cylinder gas with a conventional regulator and control.

Temperatures were measured by thermistor probes wired into a bridge circuit fed at a constant potential. A bridge circuit rather than a simple resistance measuring circuit was used to obtain a better linearity of the calibration curve. The bridge was adjusted so that the temperature within the range used could be read approximately directly with an equivalence of 10 mV/°C. Thermocouple-activated indicators were used to read inlet and outlet electrolyte temperature. The outlet temperature signal fed a controller that activated a cell drain solenoid valve under overtemperature conditions. A turbine-type flowmeter was used in the conditioning water flow line, and this gave visual indication as well as a signal for the recorder. A visual flowmeter was used to indicate the electrolyte flow rate. The electrolyte flow rate was not recorded since it was intended that the flow rate be constant during any one test.

The total hydrogen evolved from the cell is an indication of the efficiency with which the lithium anode is being consumed; hydrogen from the cathode can be readily

calculated from the current passed, and the difference between this value and the total volume of hydrogen results from the direct action between the anode and the electrolyte. Hydrogen from the cell was passed through a wet gas meter for a visual indication of accumulated gas volume. This wet gas meter had been altered and fitted with a toothed wheel instead of the pointer. When rotating, the toothed wheel interrupted the coupling between a solid-state light source and detector, and the pulses so formed were processed so that a voltage readout could be fed to the recorder to indicate the volume of hydrogen passed through the meter.

Signals from all sources were fed to a digital recorder system that recorded the values on printed tape along with the time and a channel identification number. The recorder was set to sweep all data channels every 2 min. In addition, manual operation allowed the recording of open-circuit voltages or values immediately after a load change.

Figure 4 is a layout of the instrumentation used on the test cell. Figures 5 and 6 show the test cell with its temperature sensors and the test stand and instrumentation.

Calculations may be made using experimental data to obtain power output and losses, lithium utilization, and heat removed from the cell. In addition, resistance losses within the cell are of interest in designing cells and batteries. A computer program was developed that computed these values as well as values related to electrolyte resistance during a particular current sequent. The latter values were based on a computation of the electrolyte resistance when the LiOH concentration and the electrolyte temperature were known. Values for the heat developed within the cell could be calculated but the values obtained did not appear significant because cooling water flow rate and temperature differential could not be measured experimentally with sufficient precision to make the calculation valuable. In addition, heat losses from the cell by radiation and convection could not be readily measured. Lithium utilization values and resistance free cell potential could be calculated by the program, and significant values were obtained.

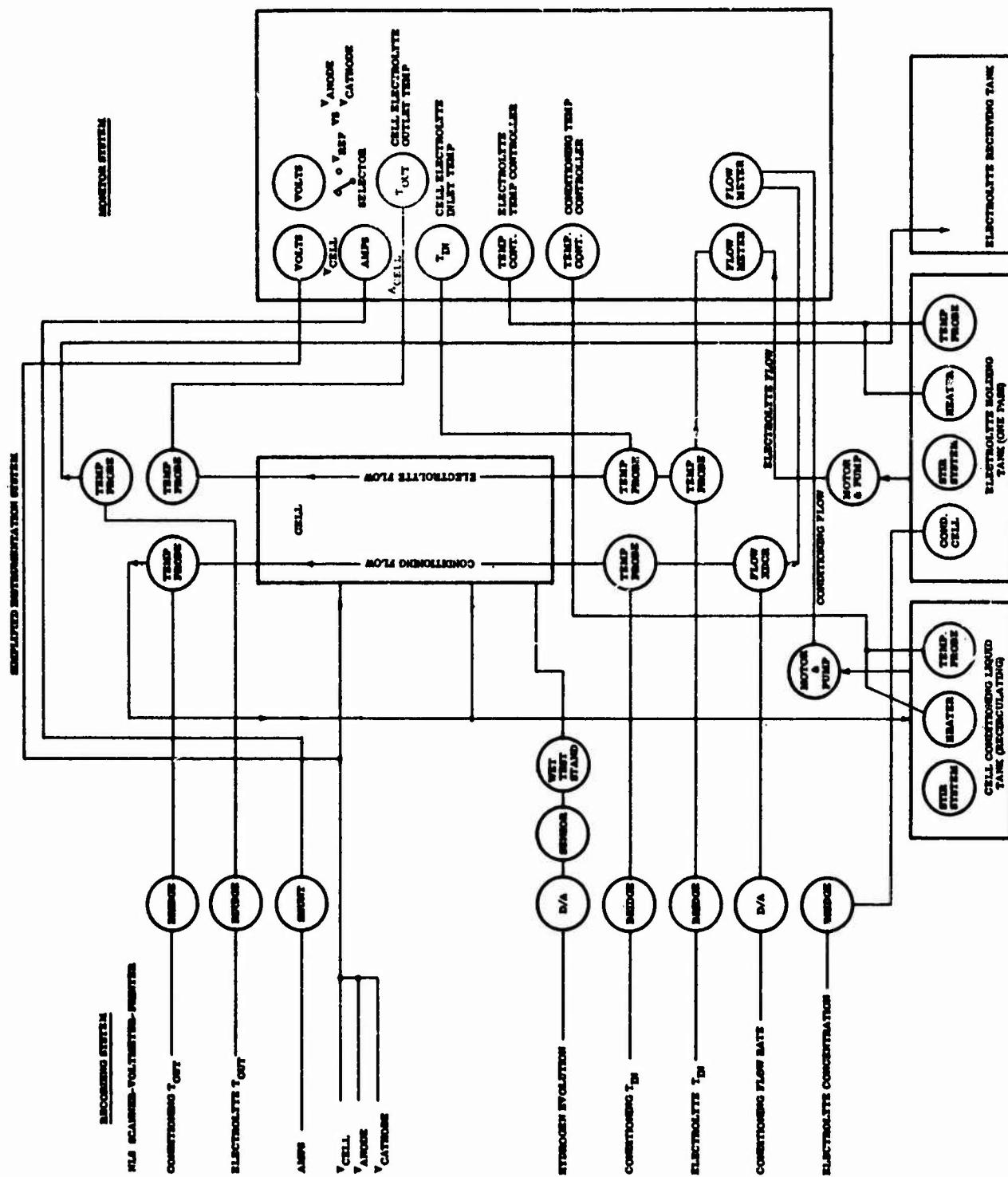


Figure 4. Test Cell Instrumentation Layout

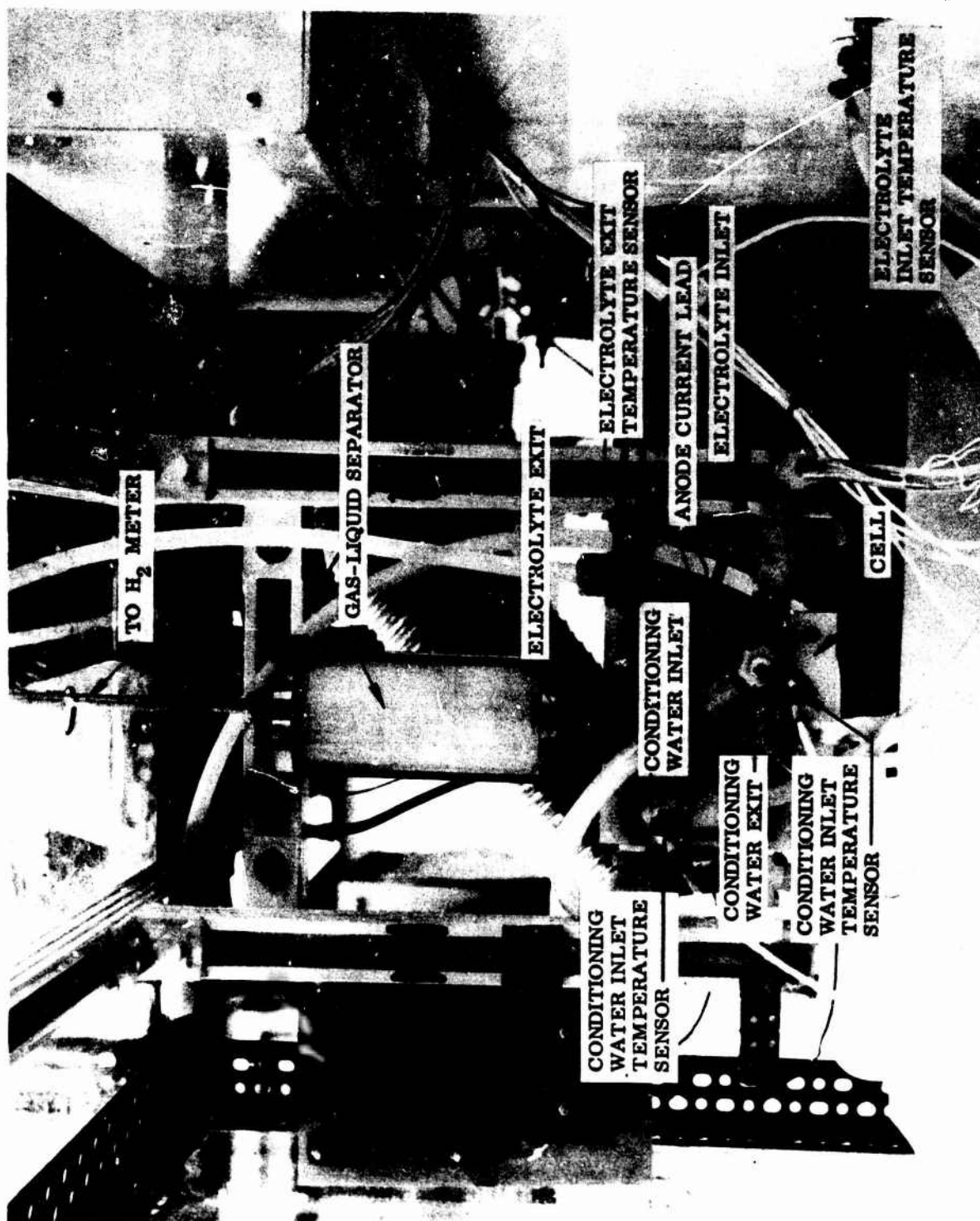


Figure 5. Test Cell and Sensors

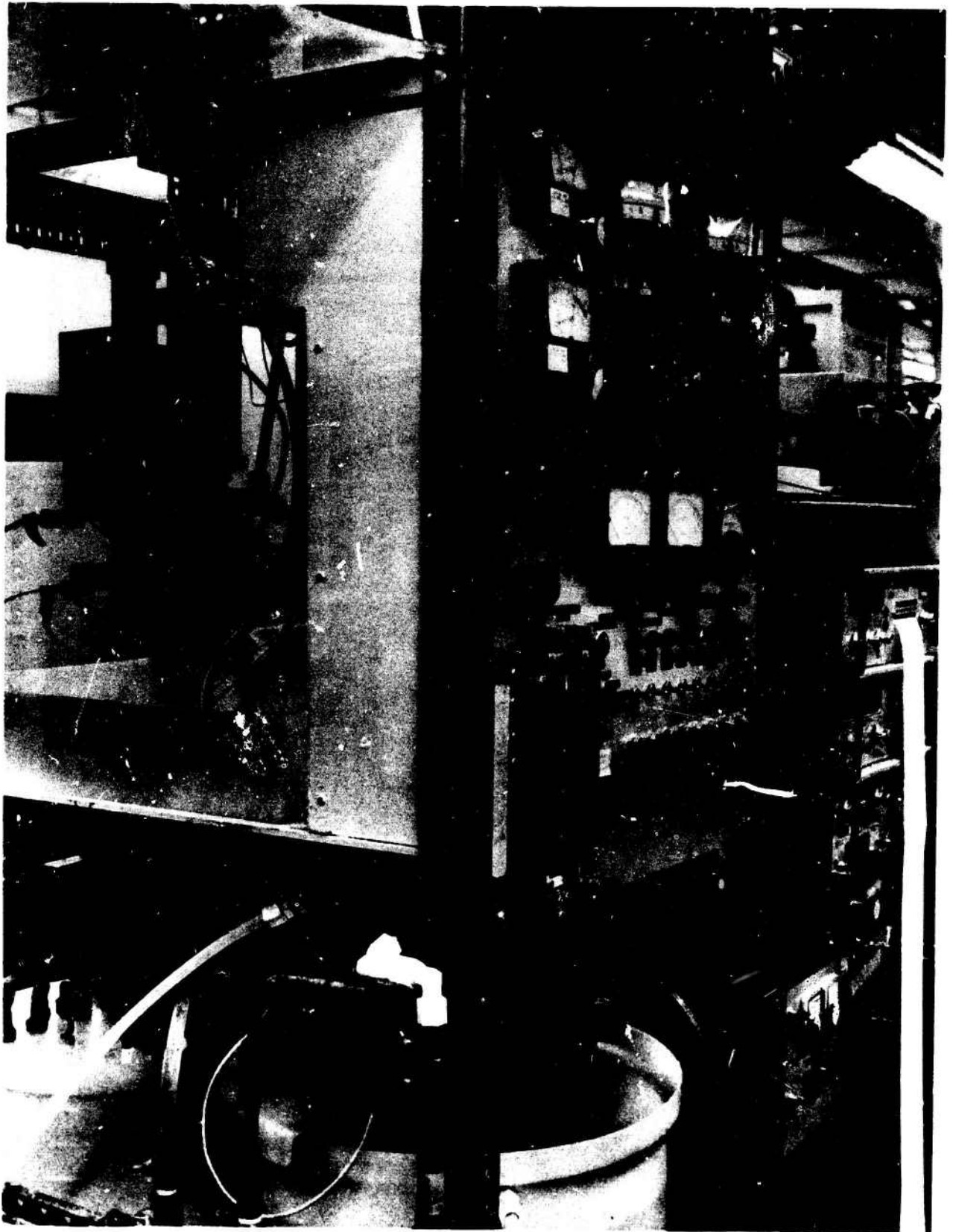


Figure 6. Test Layout With Instrumentation

Test Procedure

The operating conditions of the basic cell which are the variables to be studied include the current density, at the electrodes, the temperature of the cell, the electrolyte concentration, and the electrolyte flow rate. To consider each of these conditions as a single variable for each test would have required a prohibitive number of tests. A standard test was used in which the current density was maintained at 0.5 A/in.² increments until the cell voltage was decidedly negative, a condition which usually indicated passivation of the anode. Under normal operating conditions, 6 min of operation under a given current density was sufficient to establish stable operating conditions; when the current density approached a limiting value, the cell potential dropped during the 6-min operating time, but that value taken after 6 min was used as the comparative value.

During a typical test, the cell was filled under a load of about 0.20 A/in. and the load then removed for sufficient time to obtain an open circuit reading. The constant current load was then imposed in steps as previously outlined. Measured values were recorded every 2 min with an additional reading immediately after a current change. Values for hydrogen evolution rate were generally obtained between the fourth and sixth minute of operation at a given load level. After operation under load, the cell was open-circuited for additional measurements, and the electrolyte was then drained. The anode was removed from the cell and examined to determine whether there was evidence of poor bonding, or whether there had been sufficient edge attack to reduce the anode area sufficiently to influence the potential values under load.

BASIC CELL CHARACTERIZATION

Conductivity of LiOH Solutions

Data to calculate the conductivity of LiOH solutions had been obtained during previous work at the Lockheed Palo Alto Research Laboratory and are included here as Figure 7 because of the importance of these values to the present effort. The conductivity of

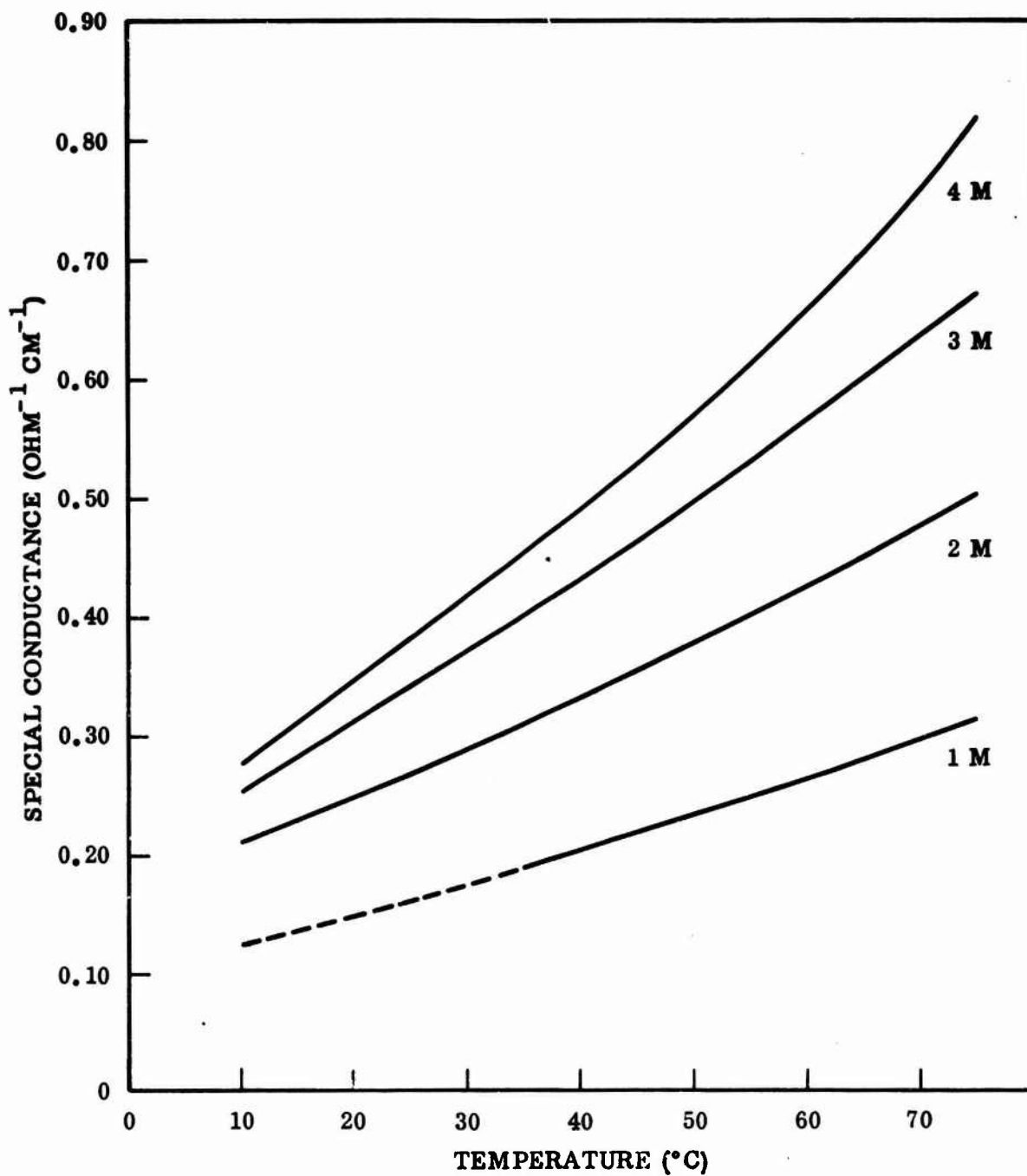


Figure 7. Specific Conductance of LiOH Solutions

the electrolyte is important because it is directly related to the potential losses that occur in the electrolyte during cell discharge. The concentration of LiOH in the electrolyte may be determined by simple acid-base titration using HCl solution. With the relationship established between concentration and conductivity, quantitative values may be calculated for the losses in the cell when the area between electrodes and the spacing between electrodes are known. The potential loss may be calculated as the cell is being discharged because the lithium depletion rate and the consequent increase in cell electrode spacing are directly related to the total measured value of hydrogen released from the cell. Gas evolved in the cell and carried in the electrolyte would decrease the conductivity of the electrolyte, but no effort was made to compensate for this factor because the location of the gas bubbles and their size were unknown.

Cell Tests With 1.0-M LiOH Electrolyte

The direct reaction between lithium and water in an aqueous electrolyte would be expected to decrease as the concentration of LiOH in the electrolyte was increased; this has been shown experimentally to be true. Because it is a chemical reaction, its rate would also increase with temperature. For this reason, electrolytes with 1-M LiOH concentration were tested only in cells at temperatures of 90°F and below. As shown in Figure 8, the electrochemical utilization of lithium was poor in this electrolyte, particularly as the temperature was increased. The flow rate of the electrolyte had little effect on the utilization of lithium. With such a low concentration of LiOH initially present, the increase in concentration by reaction even at the lowest flow rate is not sufficient for the utilization to be increased substantially.

The potential of the cell under load would be expected to increase as the temperature is increased. As shown on Figure 9, cells with 1-M LiOH electrolyte follow this pattern when the current density is high enough. At lower current densities, the cell potential decreases as the temperature is increased. This decrease is probably due to the high rate of hydrogen evolution from the cell (as shown by the poor lithium utilization) that sufficiently masks the electrodes and increases the electrolyte resistance so that the effective current density on the electrodes unshielded by gas bubbles is higher than

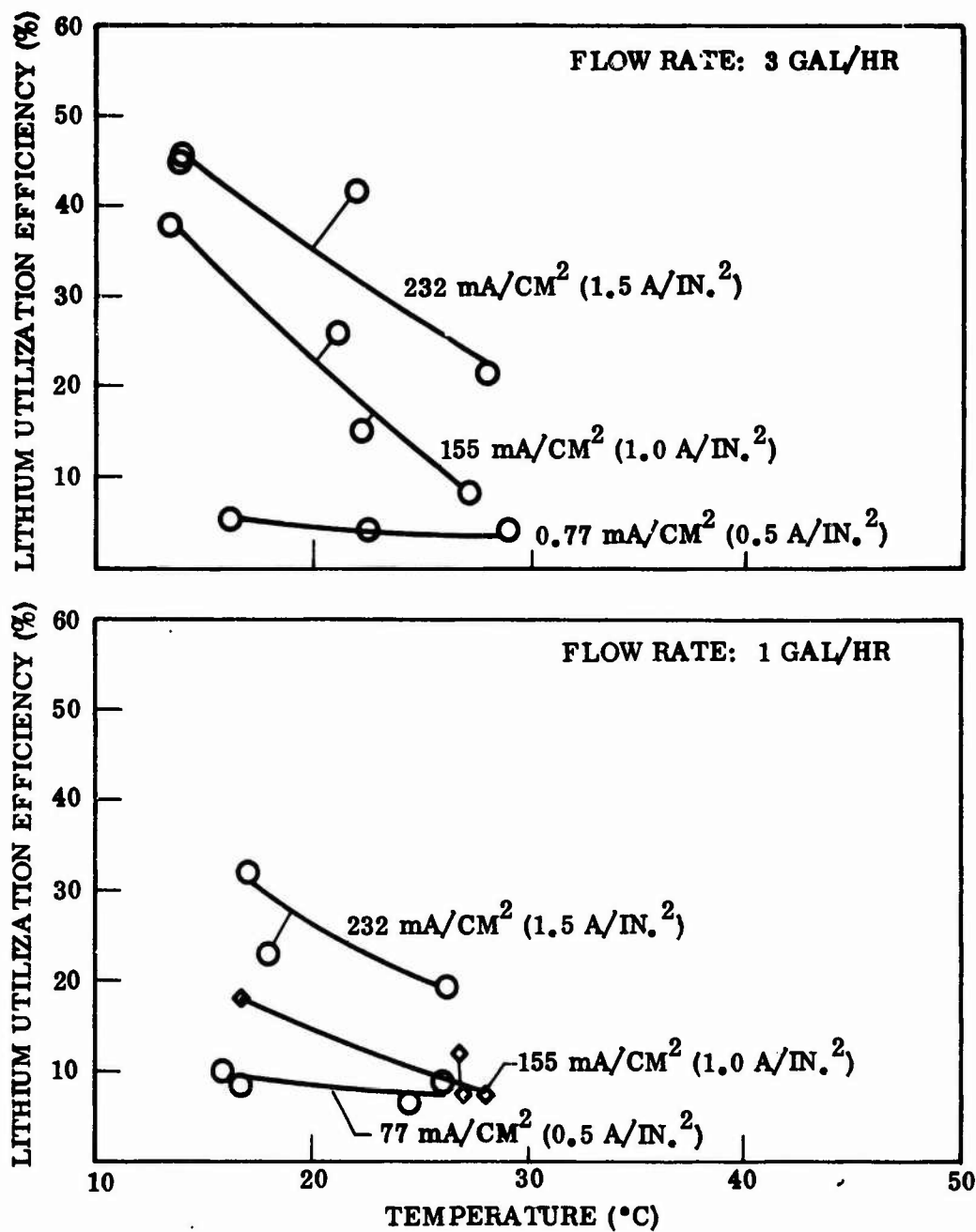


Figure 8. Lithium Utilization Efficiency in 1-M LiOH Electrolyte

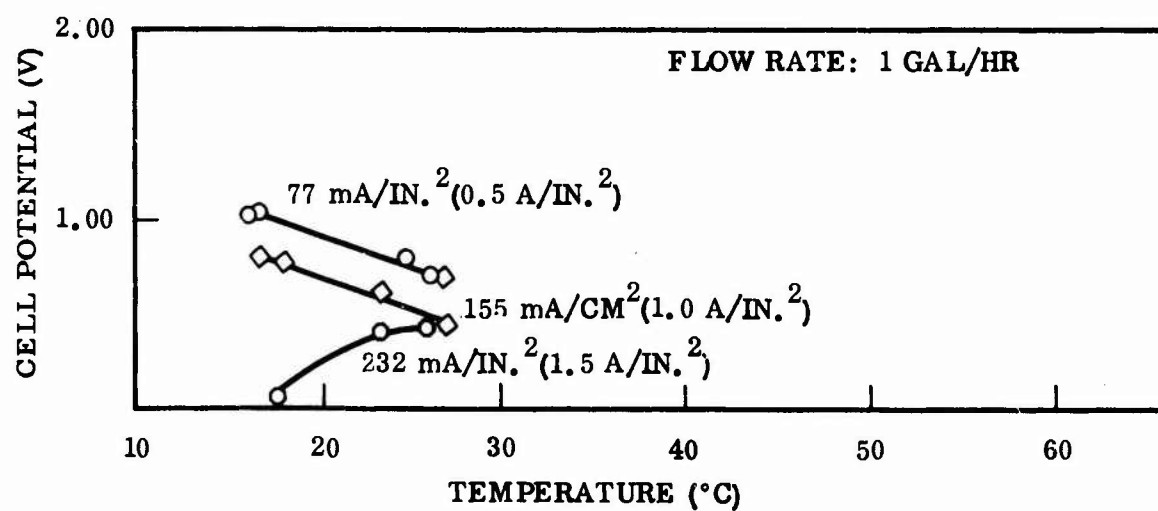
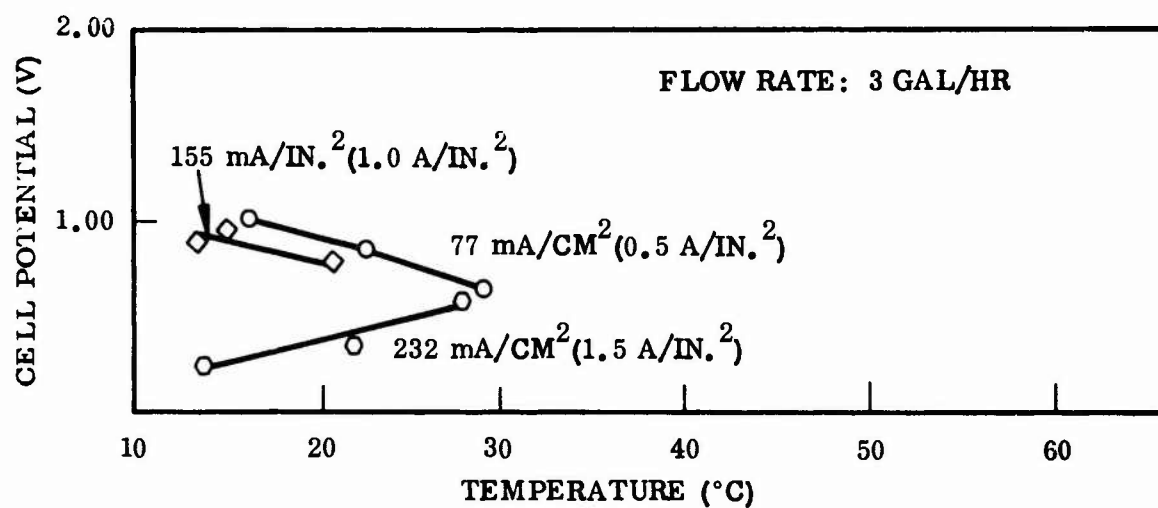
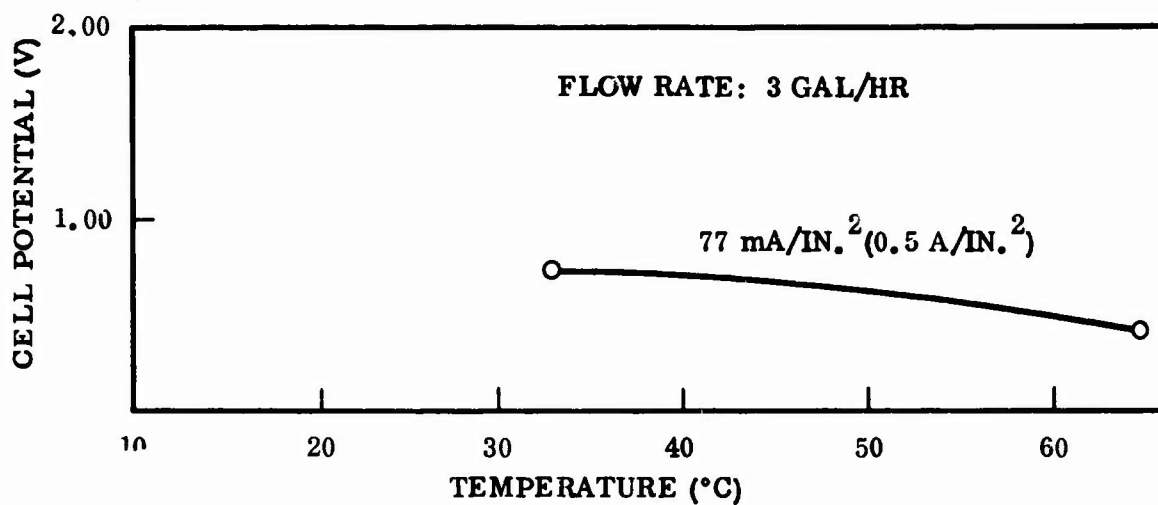


Figure 9. Voltage of Cells With 1.0-M LiOH Electrolyte

indicated. This high hydrogen rate would also increase the potential drop in the electrolyte and decrease the indicated potential.

Cells with 1-M LiOH electrolyte did have the capability of discharging at higher rates than those with more concentrated electrolyte, as will be discussed later. The high gasfing rate and the low lithium utilization, however, are a decided disadvantage. To meet the goals of the present effort, a less active electrolyte appears to be necessary.

Cell Tests With 2.5-M LiOH Electrolyte

Lithium utilization efficiencies in cells with 2.5-M LiOH are shown on Figures 10 and 11. As can be seen, the utilization efficiency is influenced more strongly by the current density than was the case when the electrolyte was 1.0-M LiOH. In addition, the utilization efficiency is increased as the flow rate is increased. There is no ready reason for this increase, and it may not be consistent when a greater range of flow rates is involved. The cell potential changes slightly over the temperature range as shown on Figure 12. The decrease at the lower temperature is an indication of the lower limiting anodic current density at the lower temperatures. The drop at the higher temperatures is probably the result of the heavy anodic gas evolution which obscures the anode surface and reduces the reactive area. The actual current density is then higher than the indicated current density. Results obtained with cells operated with 2.5-M LiOH electrolyte were quite encouraging since there is a wide operating area of temperature and current density where the lithium utilization is over 50 percent and the cell potential is above 1 V.

Cell Tests With 4.0-M LiOH Electrolyte

As expected, lithium utilization efficiency increased when 4.0-M LiOH was used as the cell electrolyte, as shown on Figure 13. The current densities that could be imposed, however, were limited to 0.5 A/in.^2 before anode passivation occurred. At the lowest flow rate, this efficiency could be extended to the higher temperatures. The potentials realized from the cells with this electrolyte were low, as shown on Figure 14. At low current densities, discharges are possible at temperatures to 165°F with reasonable control, although lithium utilization is still inefficient.

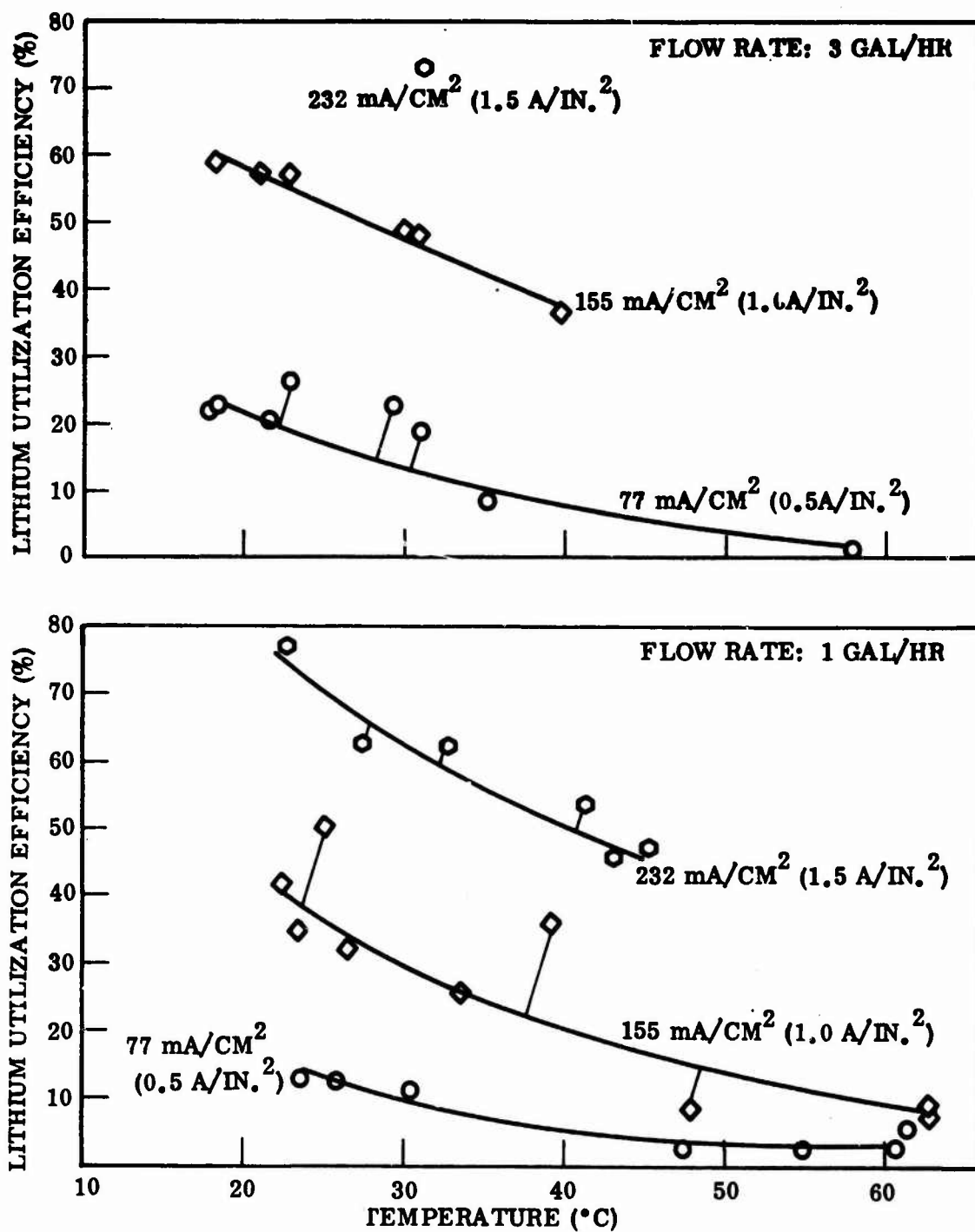


Figure 10. Lithium Utilization Efficiency in 2.5-M LiOH Electrolyte

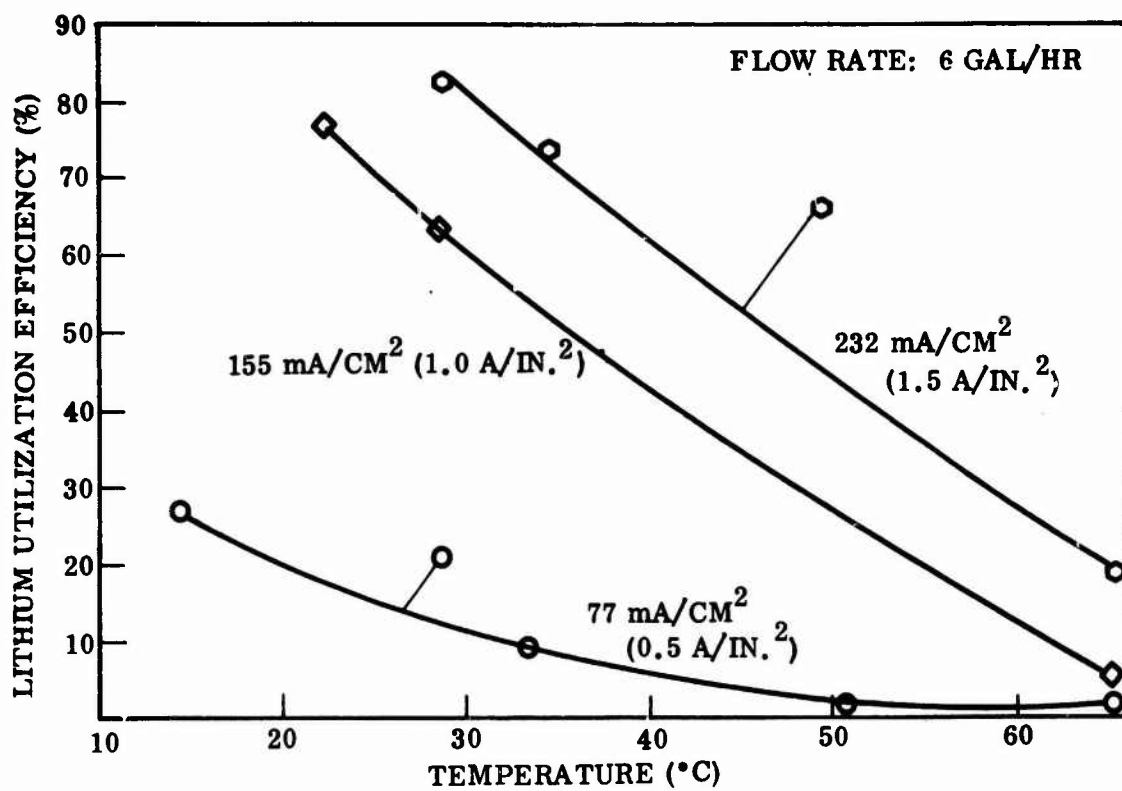


Figure 11. Lithium Utilization Efficiency in 2.5-M LiOH Electrolyte

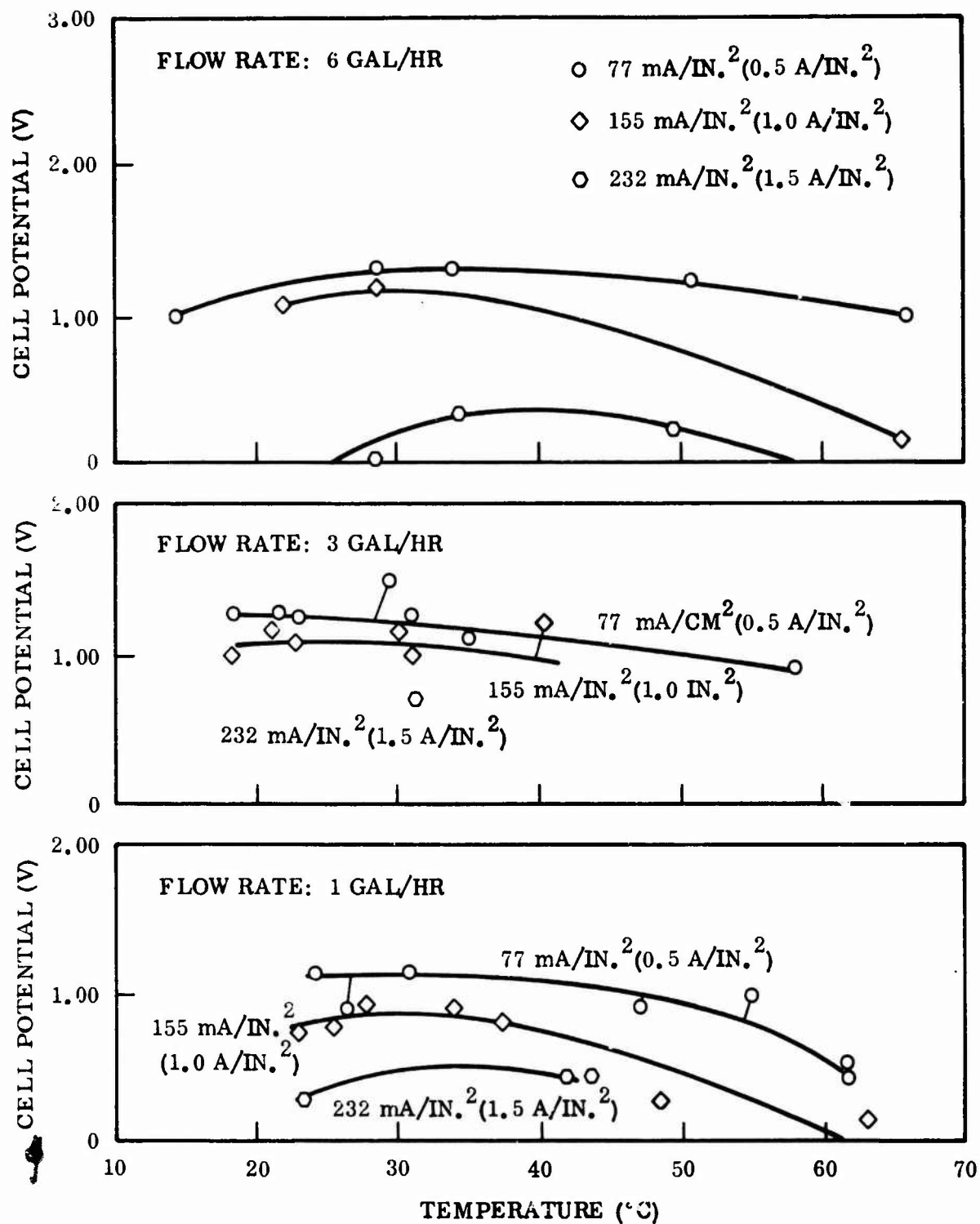


Figure 12. Voltage of Cells With 2.5-M LiOH Electrolyte

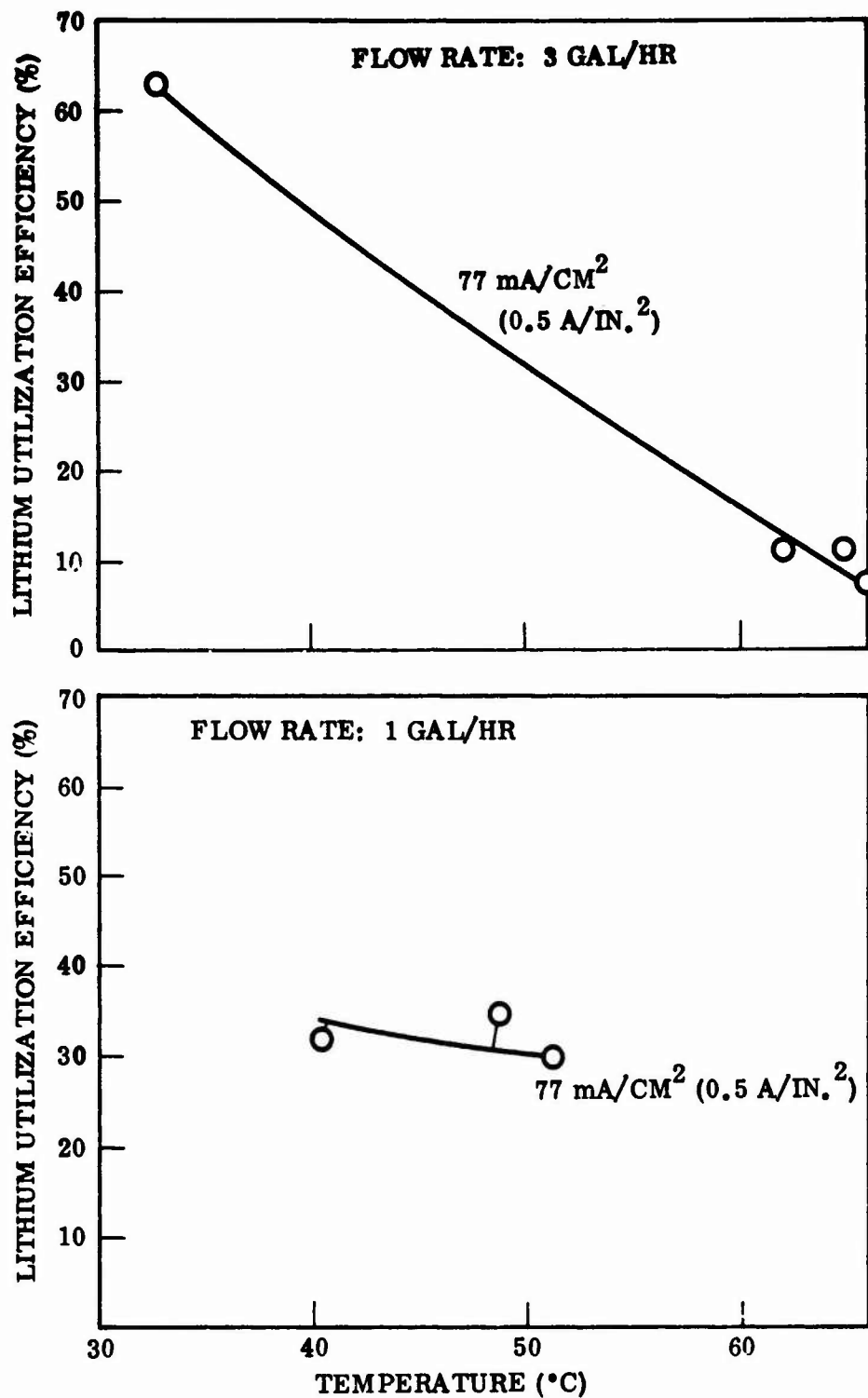


Figure 13. Lithium Utilization Efficiency in 4.0-M LiOH Electrolyte

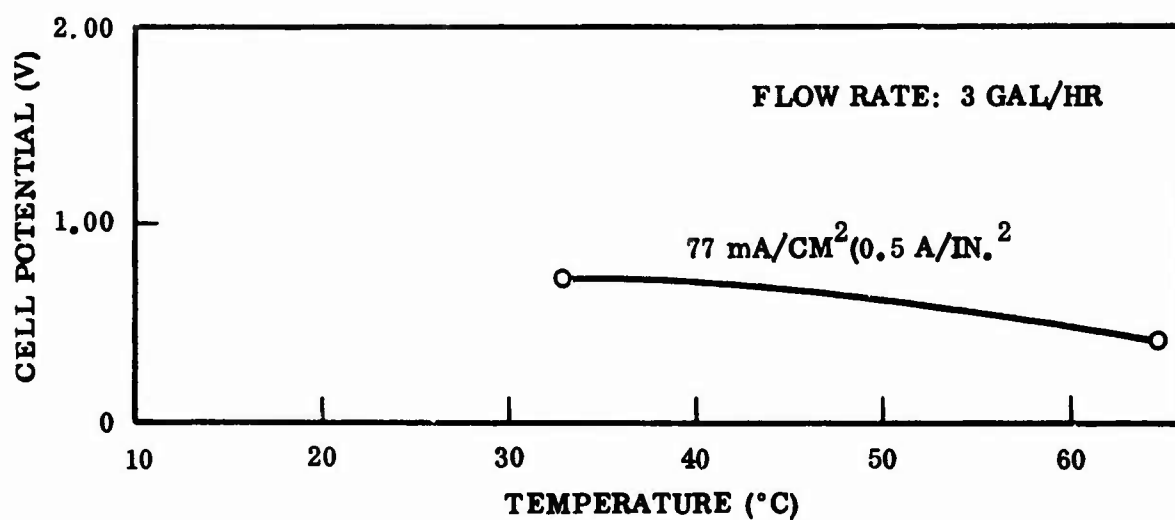
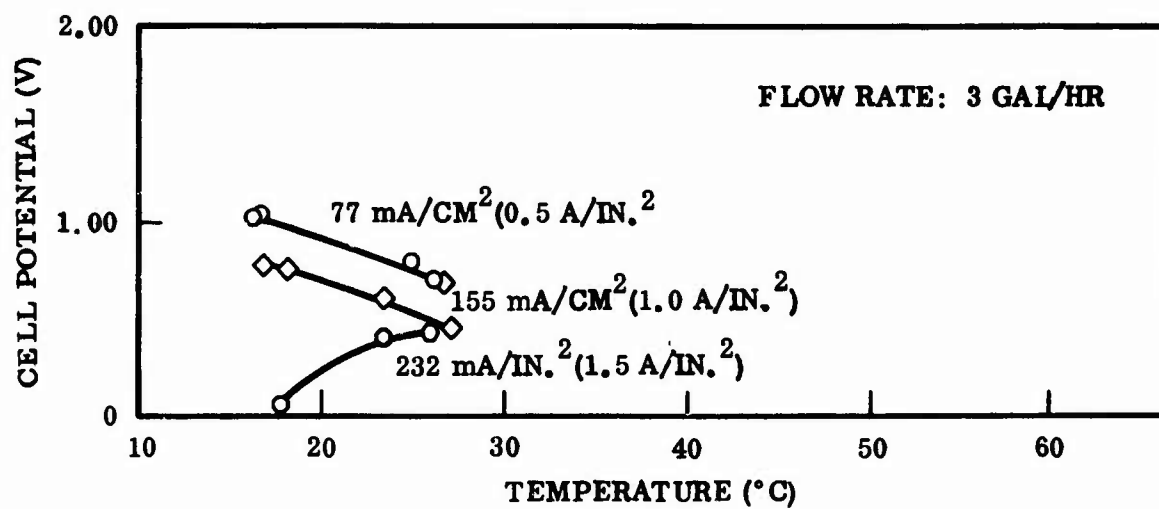


Figure 14. Voltage of Cells With 4.0-M LiOH Electrolyte

Summary of Basic Cell Characterization

The open circuit of lithium-water cells filled with electrolyte under no-load conditions are commonly above the theoretical 2.19 V because of adsorbed cathodic material. When activated under minimum load and then placed on open circuit, the cell potential is 1.90 to 1.95 V. This potential is basically that of the lithium anode under the electrolyte concentration and temperature when the hydrogen is taken as zero. When a load is impressed on the anode, the polarization increases gradually until the limiting current is realized or passivation occurs. This point is related to temperature, the electrolyte, and the time at which the electrode is held at a given current density.

In the basic cell studies with flowing electrolyte, the flow rate has an effect also. Typical of passivation, there is hysteresis when the load is reduced and the passivating film affects subsequent discharge. The cathode contrary to the anode shows an immediate rapid polarization when current is withdrawn from the cell and is the cause of loss of cell voltage when the load is first impressed.

After this immediate polarization of 0.3 to -0.4 V, the increase in cathodic polarization is very slight to current densities of over 4.0 A/in.². The cell operation is substantially dependent upon the maximum current density under which the anode can be operated. The maximum current density with 1.0, 2.5, and 4.0-M LiOH electrolyte, as dependent upon temperature, is plotted on Figure 15. These are not precise values but are estimated from the point of passivation observed on cell tests. It can be seen that the electrolyte LiOH concentration has a major effect on the current density that can be supported by the cell. Of course, this also has a significant effect on the lithium utilization which is important not only because of the excess lithium which is consumed but also because of the additional heat developed within the cell by the parasitic reaction.

In the cell configuration used for these basic characterization tests, optimization of the involved parameters of voltage, current density, and lithium utilization efficiency will be achieved at electrolyte LiOH concentrations of 2.5 to 3.5 M and will be operable to temperatures to 32°C. The flow rate will have an effect upon the experimental values,

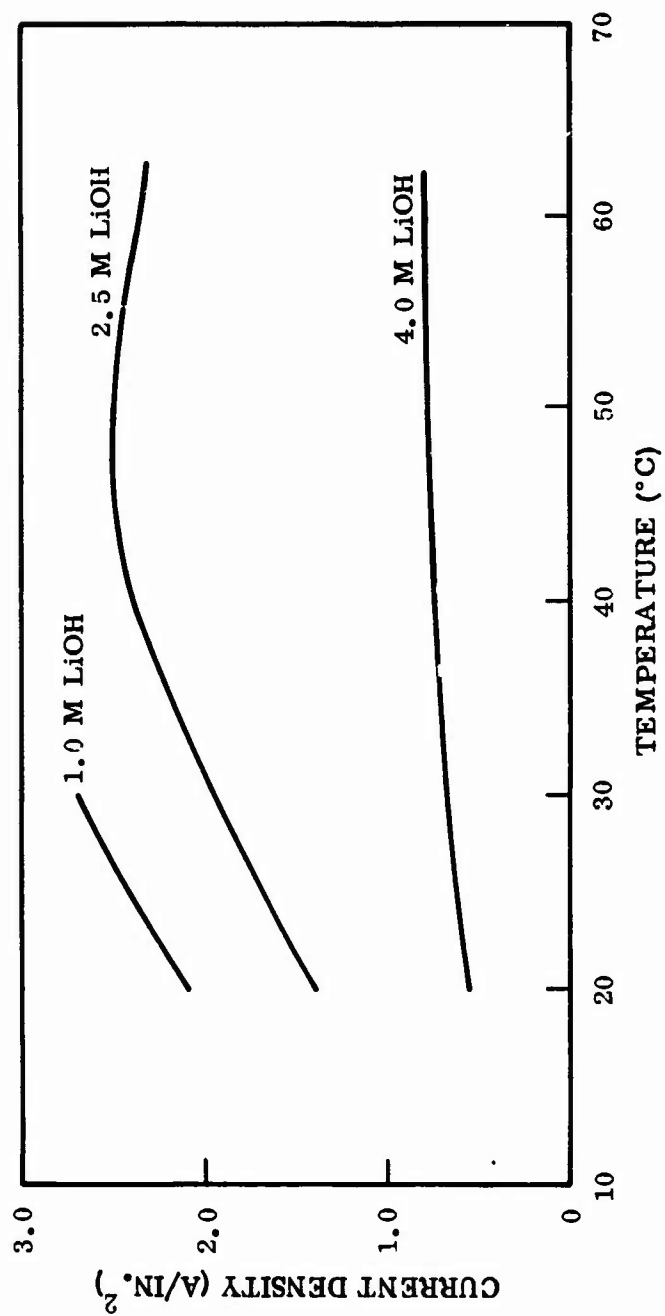


Figure 15. Maximum Current Density With Electrolyte Flow of 3 gal/hr

dependent upon the flow geometry of the cell being operated. General experience has been that increased flow improves cell characteristics until some value is reached, after which the operation is no longer flow-dependent.

INVESTIGATION OF ELECTROLYTE ADDITIVES

Organic Solvent Additives

The use of organic solvents as diluents for the electrolyte attacks the problem of lithium utilization by reducing the water concentration of the electrolyte and consequently the direct reaction between lithium and water. There is also the possibility of reduction of solvent at the cathode during cell operation. Materials that were considered as additives are those solvents that have mutual solubility with water and that have low reactivity with lithium. The materials must also be stable in strongly alkaline solution and have a high boiling point for possible operation at high temperatures. The materials that were considered are listed on Table 2, together with some of their physical properties.

TABLE 2. PHYSICAL PROPERTIES OF ORGANIC ELECTROLYTE ADDITIVES

Material	Freezing Point (°C)	Boiling Point (°C)	Viscosity	Specific Gravity	Solubility and Water
Ethylene Glycol	8	197.3	14.9	1.10	Complete
Glycerine	17.9	290	—	1.26	Complete
Isobutyl Alcohol	-89	99.5	—	0.81	125 g/liter
Diacetone Alcohol	-42.8	169.2	3.2	0.94	Complete
Butyl Cellosolve (2-Butoxyethanol)	<-100	171.2	—	0.90	Complete

A reduction in direct lithium-water reaction was achieved in practice with these solvents. It was apparent, however, that the solubility of LiOH in the mixed solvent was

considerably less than in water alone and that the reduced lithium solubility was reflected in cell operation. Current density of 0.5 A/in.^2 could be obtained, but higher current densities resulted in passivation of the anode. The effect of the three additives tried – ethylene glycol, glycerine, and butyle cellosolve (2-butoxyethanol) – were surprisingly similar. The lithium utilization rates with these solvent additives are plotted in Figure 16. The lithium efficiency is about twice that obtained in straight water solutions. Improved lithium utilization was obtained with 2.0-M LiOH in 25-percent glycerol, but this appeared to be maximum solubility. This amount of LiOH was not soluble in the other solvent mixtures. Because of the limited solubility and low current densities obtained on cell tests with these electrolytes, the complete program originally contemplated with them was not completed, but the effort directed toward additional work with inorganic salt additives.

Inorganic Salt Additives

Three additional electrolytes were selected for study: sodium hydroxide, potassium hydroxide, and lithium chloride solutions. The first two were selected to decrease the parasitic lithium attack by maintaining a high hydroxyl ion level in the solution but with the hope that the passivation current density would not be decreased proportionately. The lithium chloride was selected as a salt that would reduce the water activity of the solution and that would determine the effect of the added chloride ion. It was found that high concentrations of all these salts reduced the LiOH solubility excessively, and 4-M solutions were prepared for test of the hydroxides and 6.75-M LiCl. The cell potential and lithium utilization efficiency of cells with 4-M KOH electrolyte are shown in Figure 17.

The lithium utilization was similar to that obtained with 2.5-M LiOH, but the potential was appreciably higher. At a current density of 1.5 A/in.^2 , the potential was still above 1 V at intermediate temperatures. However, metal fire was experienced when a cell with this electrolyte was operated at high temperature, and other experiments indicated that this electrolyte should be used with considerable caution where there was a chance of anode dehydration.

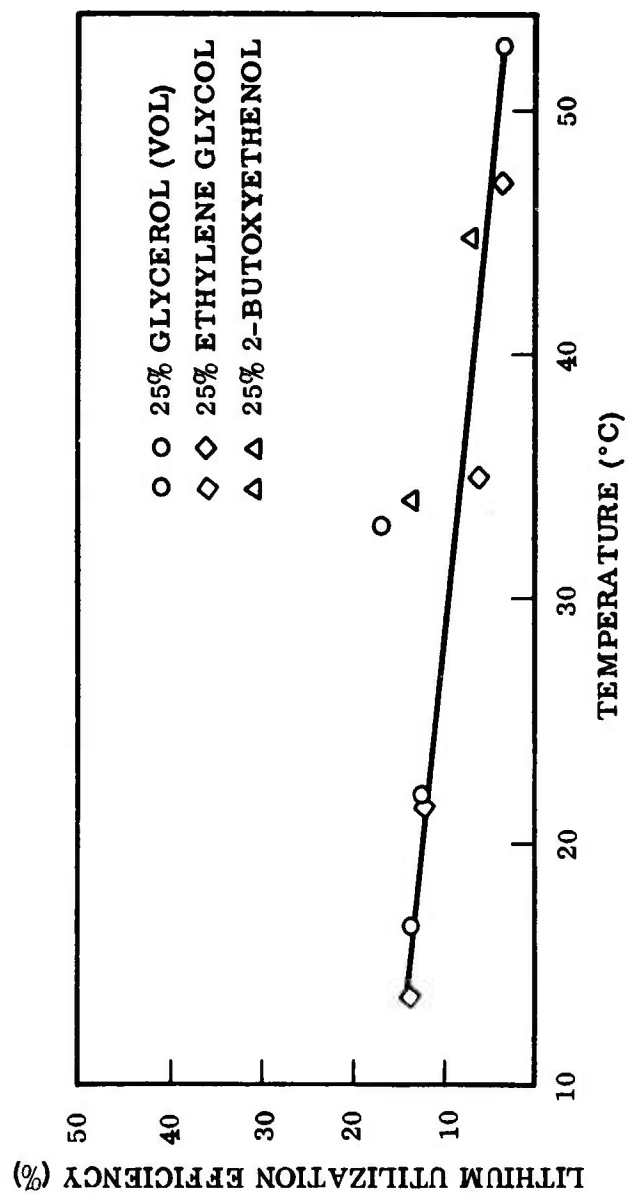


Figure 16. Lithium Utilization Efficiency in 1-M LiOH Electrolytes With Added Solvents

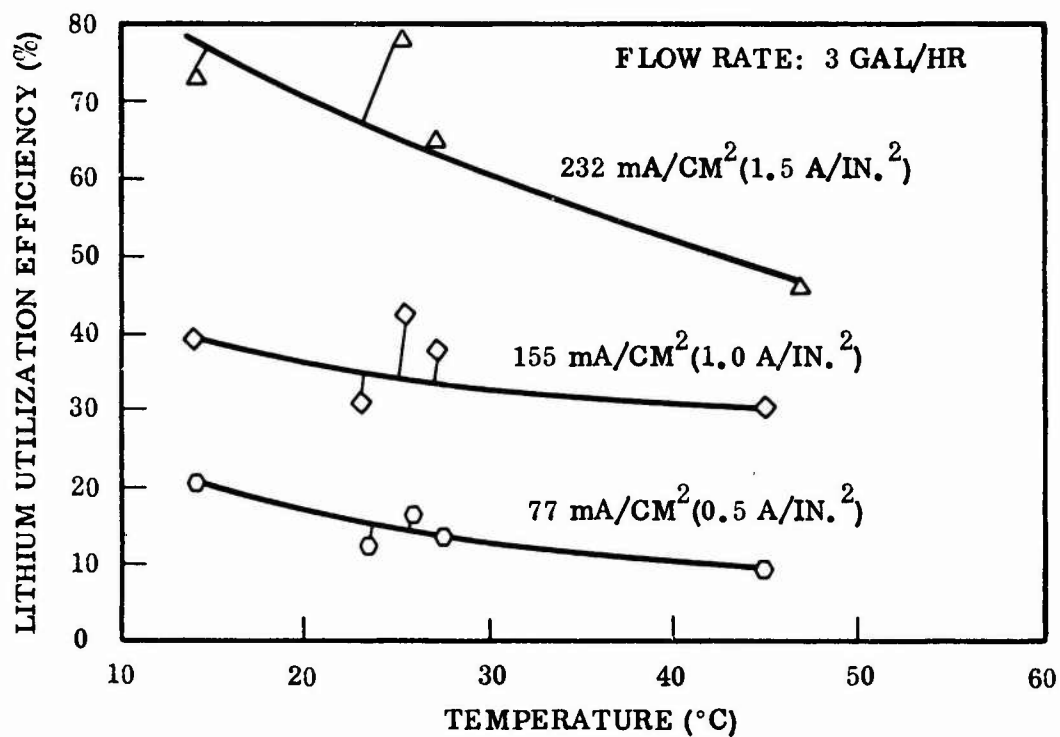
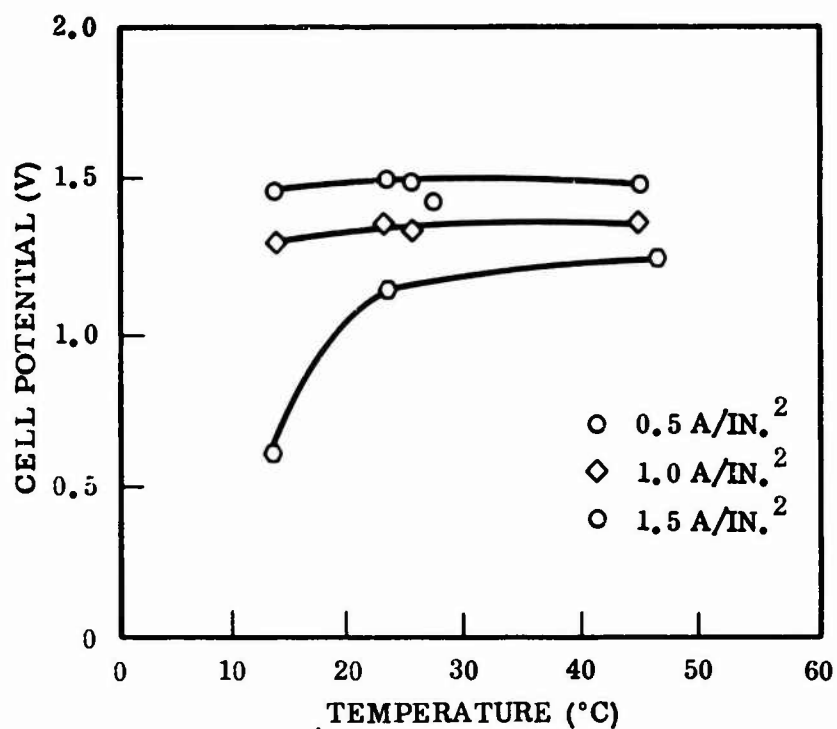


Figure 17. Cell Potential and Lithium Utilization Efficiency for Cells With 4-M KOH Electrolyte

Cells with 4-M NaOH electrolyte showed high efficiency at the lower temperature, which decreased rapidly at 30°C to a plateau that extended to 50°C and then fell off, as shown in Figure 18. It was similar to that with 4-M KOH electrolytes at mid-temperature but better below 30°C. Its cell potential was slightly below that measured for cells with 4-M KOH electrolyte but much better than cells with 2.5-M LiOH.

The use of 6.75-M LiCl electrolyte in cells resulted in poor lithium utilization efficiency, as shown in Figure 19. The potential was high in the intermediate temperature range but fell off at both the top and bottom of the temperature range which was used for the tests. There was no abrupt passivation of the anode on these tests as experienced with hydroxyl electrolytes; the anode polarization increased steadily but within the range in which experiments were run did not passivate. Presumably, the activity of the chloride ion was sufficient to prevent the formation of a passivating film.

Cells were also discharged with electrolytes of NaOH or KOH with the addition of 1-M LiOH. The conductivity of such solutions is shown in Figure 20. The addition of LiOH to 4-M KOH improved the lithium utilization efficiency considerably and gave good utilization to over 50°C at the higher current densities. The addition depressed the cell potential and induced passivation at a lower current density than with the straight KOH solution. The cell potential and lithium utilization for these tests are shown in Figure 21. Results of tests with 4-M NaOH and 1-M LiOH are shown in Figure 22. The results are similar to those with KOH with slightly lower cell potential. These results with mixed hydroxide electrolytes at the higher temperatures simulate what may be expected in a cell in which KOH or NaOH-based electrolyte is used initially, the discharge reactions add LiOH to the solution, and the temperature increases during discharge.

The good efficiency achieved with NaOH and the higher passivation current density indicated for LiCl solutions suggested the use of mixed solutions. The cell potential and lithium utilization efficiency for tests with these electrolytes are shown in Table 3. Generally, the addition of NaOH to a predominately LiCl electrolyte had little effect on the lithium utilization or the cell potential. The addition of LiCl to 4-M NaOH did not

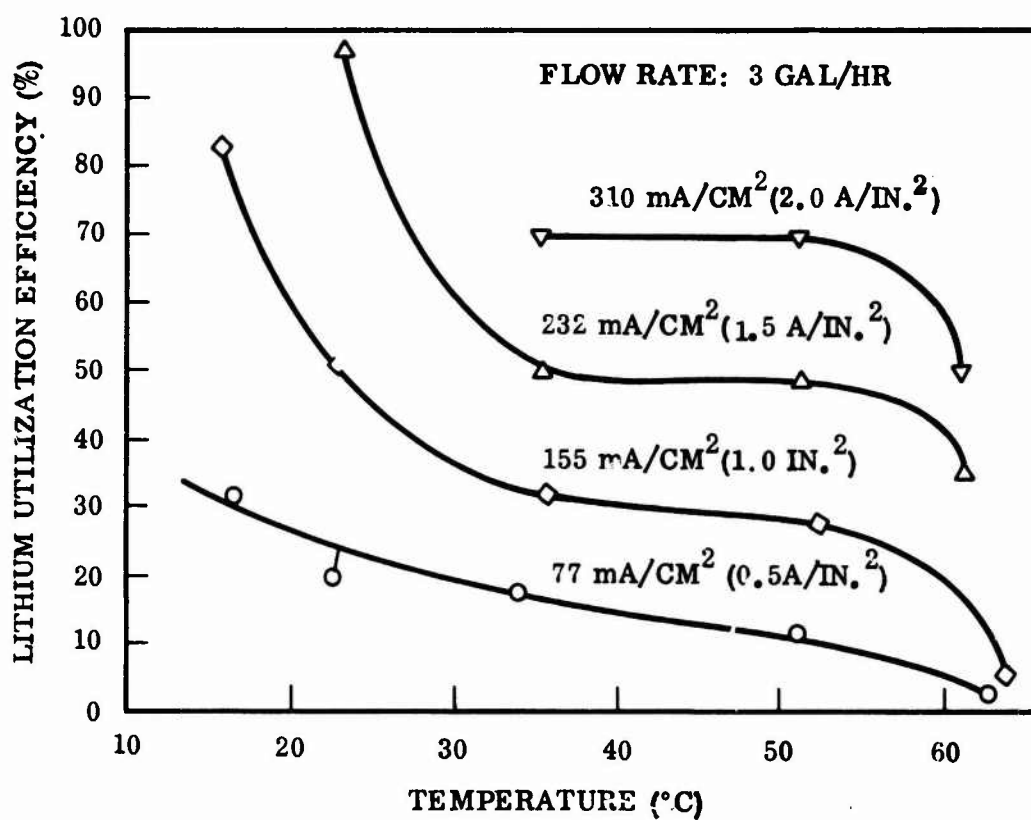
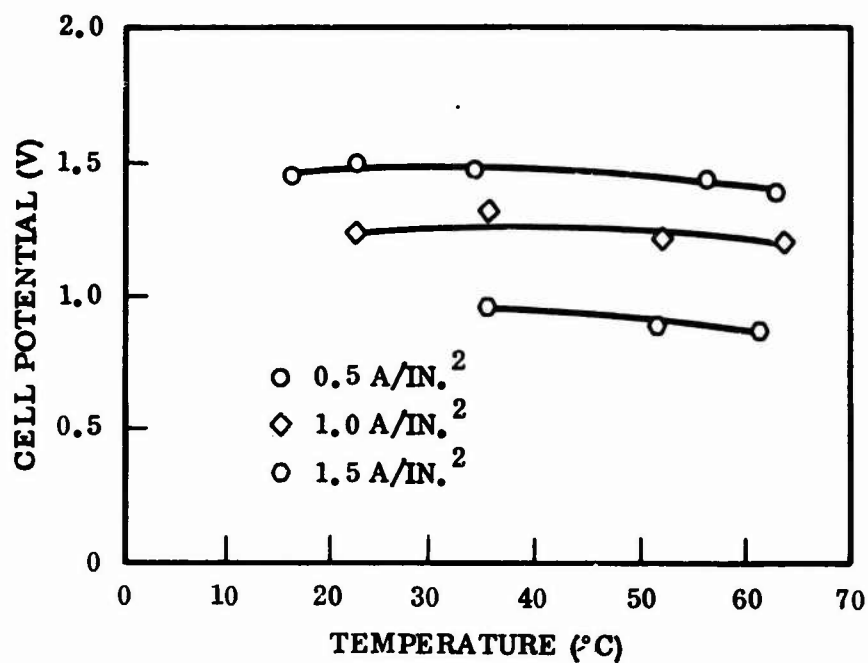


Figure 18. Cell Potential and Lithium Utilization Efficiency for Cells With 4-M NaOH Electrolyte

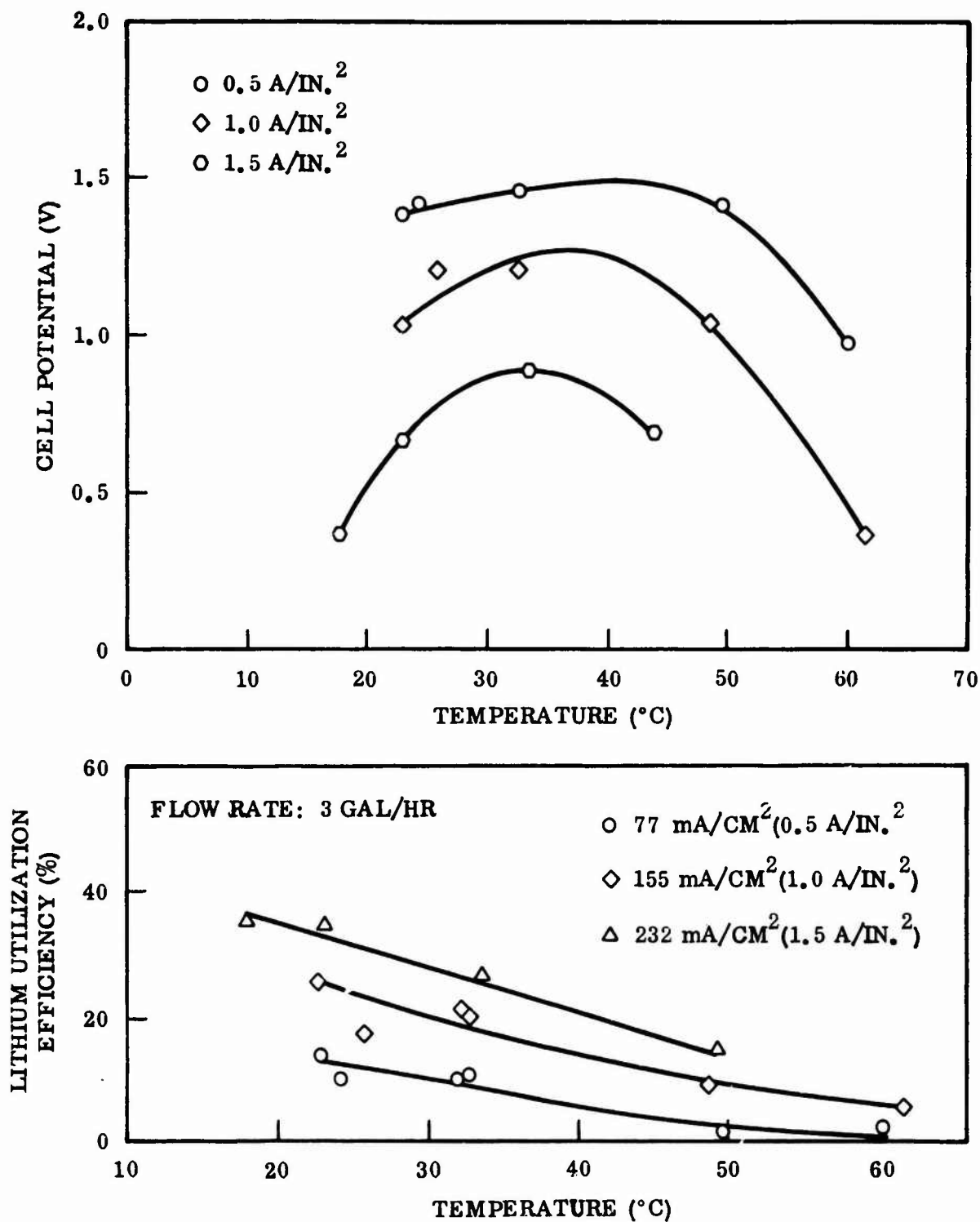


Figure 19. Cell Potential and Lithium Utilization Efficiency for Cells With 6.75-M LiCl Electrolyte

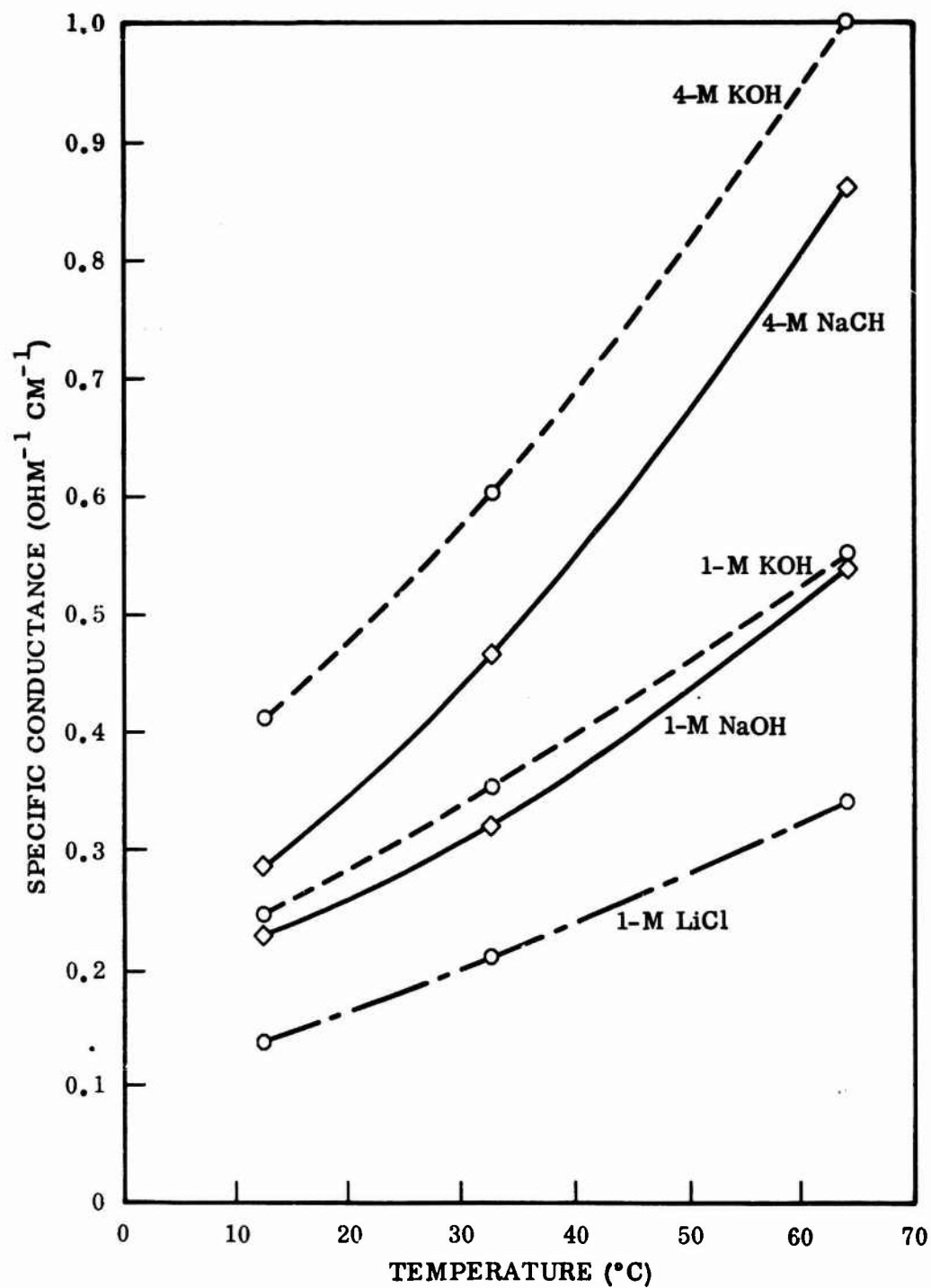


Figure 20. Specific Conductance of 1-M LiOH Solutions With Added Salts

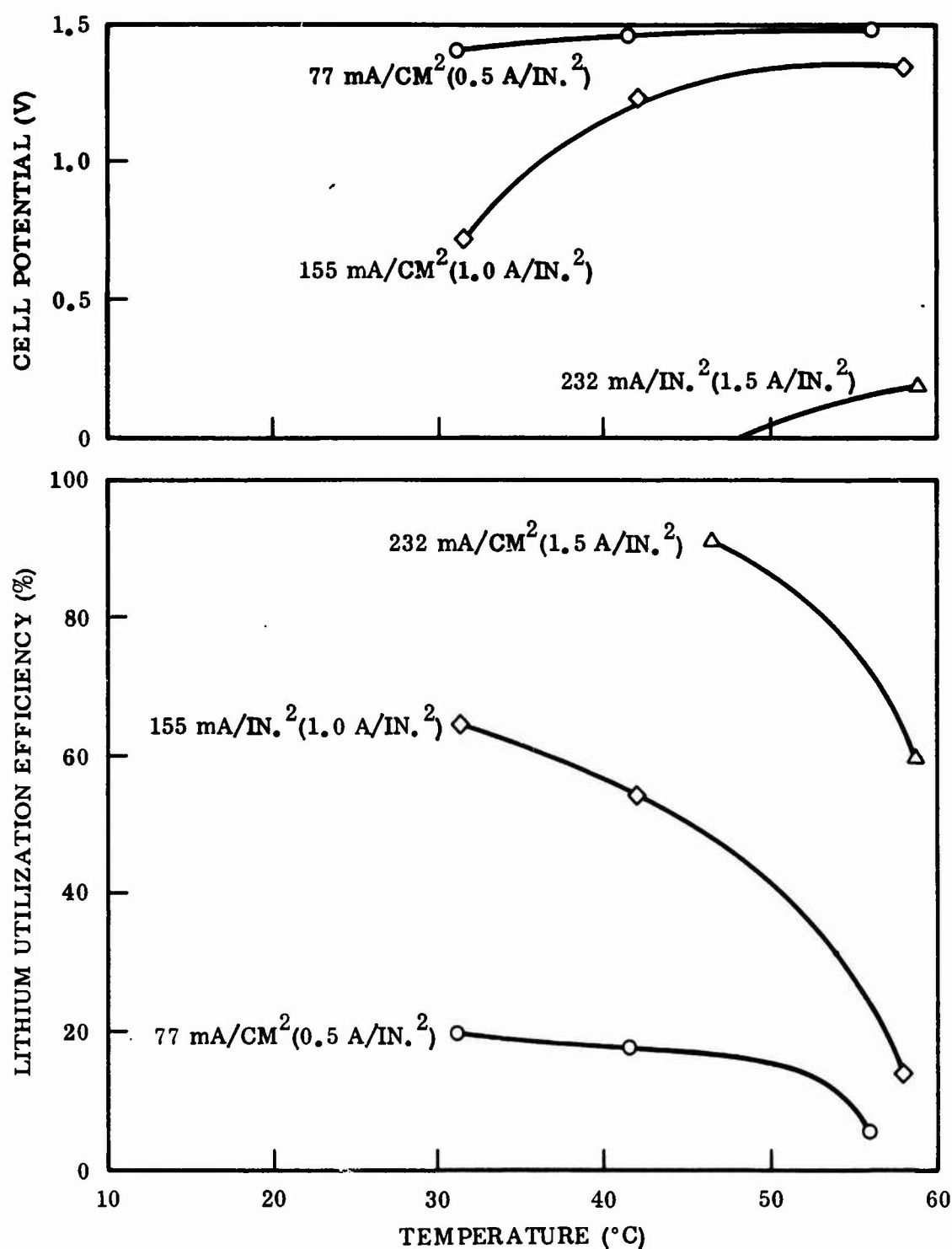


Figure 21. Cell Potential and Lithium Utilization Efficiency for Cells With 4-M KOH, 1-M LiOH Electrolyte

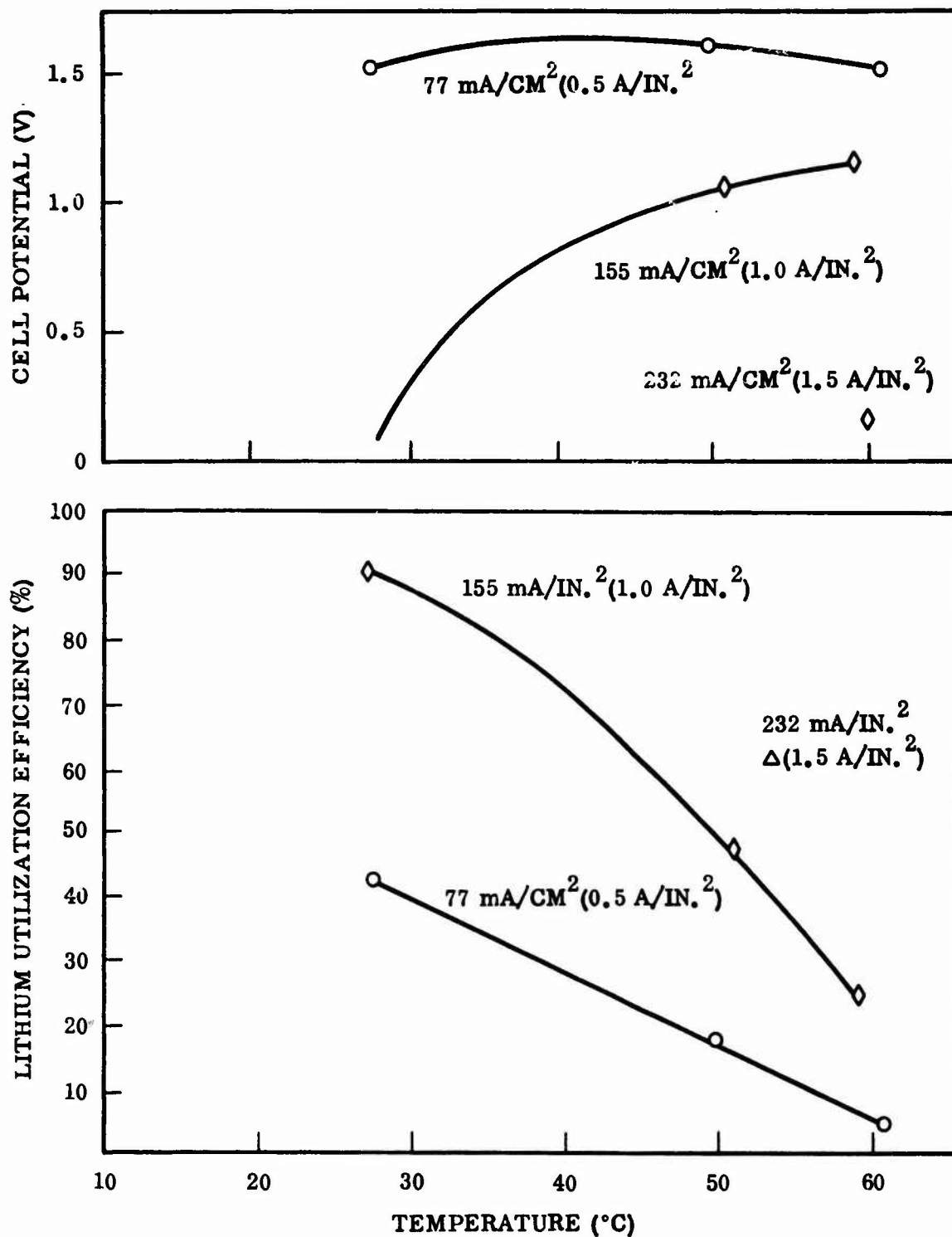


Figure 22. Cell Potential and Lithium Utilization Efficiency for Cells With 4-M NaOH, 1-M LiOH Electrolyte

extend appreciably the usable current density for a cell using that electrolyte. It did not appear to affect the lithium utilization, but it did reduce the cell potential.

TABLE 3. POTENTIAL AND LITHIUM UTILIZATION EFFICIENCY OF CELLS WITH LiCl-NaOH ELECTROLYTE AT 32°C AND WITH A FLOW RATE OF 3 GAL/HR

Cell No.	Electrolyte	0.5 A/in. ²		1.0 A/in. ²		1.5 A/in. ²	
		Cell Potential (V)	Lithium Utilization (%)	Cell Potential (V)	Lithium Utilization (%)	Cell Potential (V)	Lithium Utilization (%)
139 ^a	4-M LiCl	1.454	11	1.228	19	0.884	20
140 ^a	4-M LiCl 1-M NaOH	1.418	23	1.156	23	0.961	23
141 ^a	4-M LiCl 2-M NaOH	1.412	17	1.198	22	0.883	28
171	1-M LiCl 4-M NaOH	1.281	26	0.793	60		
168	0.5-M LiCl 4-M NaOH	1.330	15	0.630	65		
129	4-M NaOH	1.519	18	0.985	57		
170 ^b	1-M LiCl 4-M NaOH	1.381	16				
169 ^b	0.5-M LiCl 4-M NaOH	1.323	9	1.125	30	0.331	

^a Flow Rate: 6 gal/hr.

^b 49°C.

LITHIUM ALLOY ANODES

The test work originally planned with lithium-magnesium alloy anodes for this time period was delayed to take advantage of similar work being carried out on an Independent Research program at the Lockheed Palo Alto Research Laboratory.

CATHODE STUDIES

Cathodes were prepared from different metal, metal forms, or with catalyzed surfaces for comparison with a standard nickel electrode. The standard cathode used for comparison was the same as used in the basic cell characterization. This is a sandblasted plane nickel surface to which an expanded nickel metal sheet has been spot-welded to increase surface area. The iron cathode was similarly prepared with a plane iron surface to which was welded expanded iron metal mesh.

The standard nickel cathode was brush-painted with a semicolloidal graphite in an epoxy resin binder* to evaluate the effect of graphite as a cathode. The coating was brushed with a soft stainless steel brush after oven curing to reduce the surface resistance. The resistance of this coating was still sufficient to have an effect on the cell potential as measured. The porous nickel cathode was prepared from a sintered carbonyl nickel battery plaque 0.094 in. thick with about 65-percent porosity. The porous nickel was compressed in a circular area in the center so that a nickel stud could be welded in place for mounting. As a result, the electrode area was slightly reduced, and the portion of the anode facing this area was attacked less than the surrounding area. Both this porous nickel cathode and the standard nickel cathode were plated with black nickel from the same bath to study the effect of the catalytic surface.

The black nickel bath had the following composition:

74.8 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
18.70 g NH_4Cl
18.70 g ZnCl_2
9.38 g NH_4SCN
 H_2O to make up 1 liter of solution

Forty-five minutes of plating at a current density of 0.1 A/in.^2 gave an even black coating.

*Acheson Colloids Company, DAG No. 213, Port Huron, Michigan.

Black platinum was electrodeposited on test cathode surfaces using a bath of the following composition:

30 g $\text{H}_2\text{PtCl}_5 \cdot \text{nH}_2$ (40% Pt)
 1.2 g $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$
 In H_2O to make 1 liter of solution

A plating time of 1 min with a platinum anode at room temperature and a current density of 1.3 A/in.^2 yielded a dense black platinum coating on the nickel structure.

The cell voltages at various operating current densities for the cells are summarized in Figure 23 for cells at 10°C . The use of black platinum on nickel exmet cathodes yields higher cell voltages at currents densities less than 1 A/in.^2 at this temperature. The use of black nickel electroplated on nickel expanded metal structures also results in cells with improved potential over cells using bare nickel cathodes. In none of these tests was the efficiency of the lithium utilization substantially altered by the nature of the cathode surface. Other cells were used to test cathodes at 32°C and with flow rates of 3 gal/hr, as listed in Table 4.

TABLE 4. EFFECT OF CATHODE ON CELL POTENTIAL AND LITHIUM UTILIZATION - CELLS OPERATED AT 32°C WITH A FLOW RATE OF 3 GAL/HR

Cell No.	Electrolyte Cathode	0.5 A/in. ²		1.0 A/in. ²		1.5 A/in. ²	
		Cell Potential (V)	Lithium Utilization (%)	Cell Potential (V)	Lithium Utilization (%)	Cell Potential (V)	Lithium Utilization (%)
129	4.0-M NaOH Ni exmet on Ni	1.46	18	1.22	57	—	—
145	4.0-M NaOH Ni exmet on Ni graphite coated	1.39	28	1.19	47	0.44	68
154	4.0-M NaOH Fe exmet on Fe	1.41	29	0.99	43	0.87	48
147	4.0-M NaOH Porous Ni	1.65	22	1.39	51	0.33	74
148	4.0-M NaOH Porous Ni	1.63	20	1.36	48	0.35	70
153	4.0-M NaOH Porous Ni + Black Ni	1.55	23	1.06	52	—	—
151	4.0-M NaOH Ni exmet on Ni + Black Ni	1.54	17	1.39	48	0.71	75
162	4.0-M NaOH Ni exmet on Ni + Black P+	1.77	14	1.53	30	0.84	74

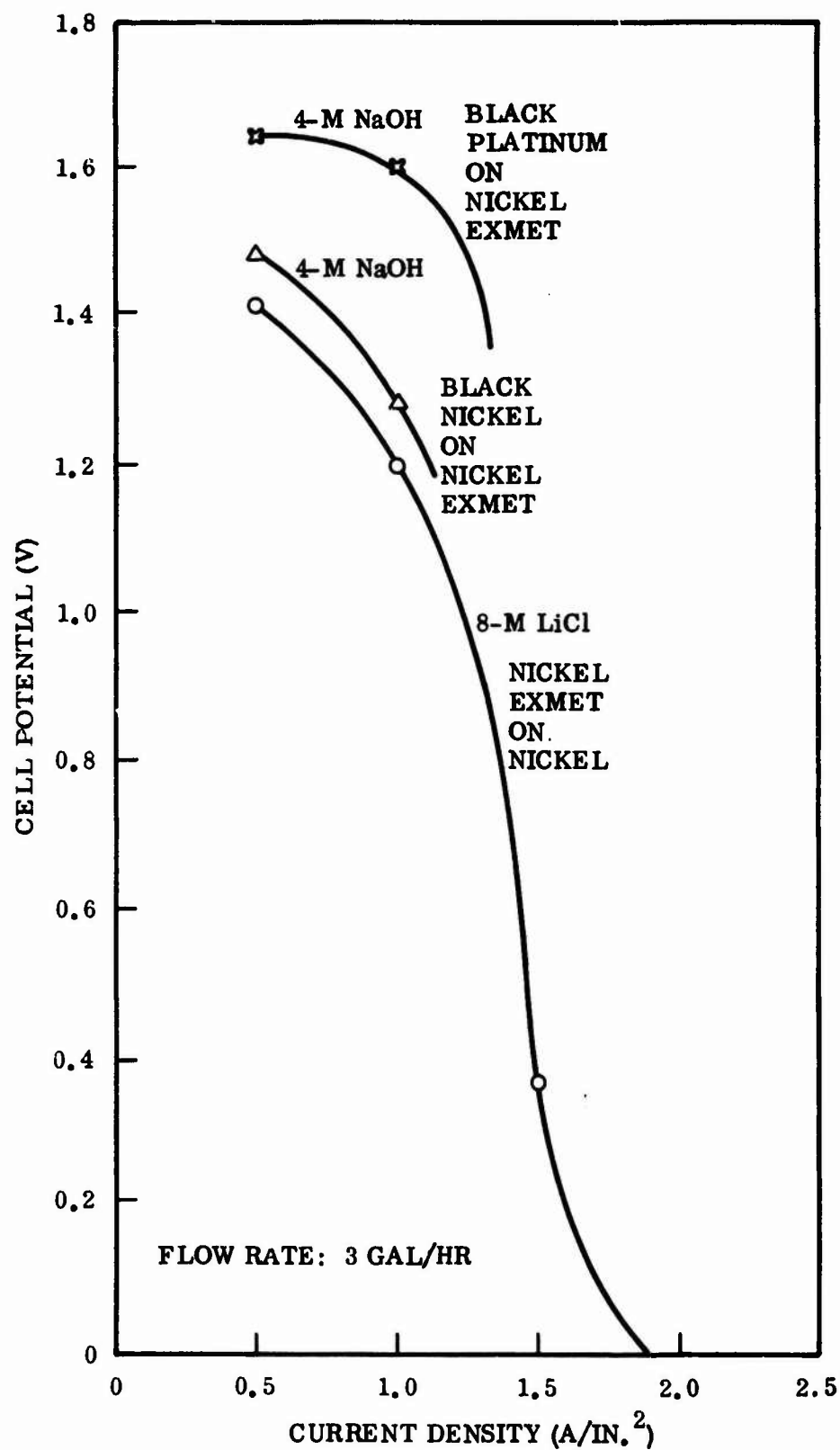


Figure 23. Effect of Cathode on Cell Potential at 10°C

The cell voltages at various operating current densities for the cells are summarized in Figure 24. Black platinum-plated electrodes with nickel-expanded metal supports were again clearly superior at current densities of 1.0 A/in.^2 or less. Nickel-expanded metal, support-plated with black nickel, yielded the next higher cell voltages below 1.0 A/in.^2 current density. The cells tested with black nickel cathodes showed improvement of at least 0.1 V in cell voltage over that obtained by the use of bare nickel-expanded metal cathodes.

The cell characteristics are controlled by the cathode structure and properties at low current densities, as shown in Figure 24. At higher current densities, the potential differences between the several cathode structures is less, and clearly the lithium anode reaction is limiting the rate of cell reaction. At both temperatures tested, structures prepared with iron or nickel were equally effective. The higher potentials obtained with the porous nickel indicate that increasing the cathodic surface area may be a simple way of increasing the cell potential without sacrifice of current density.

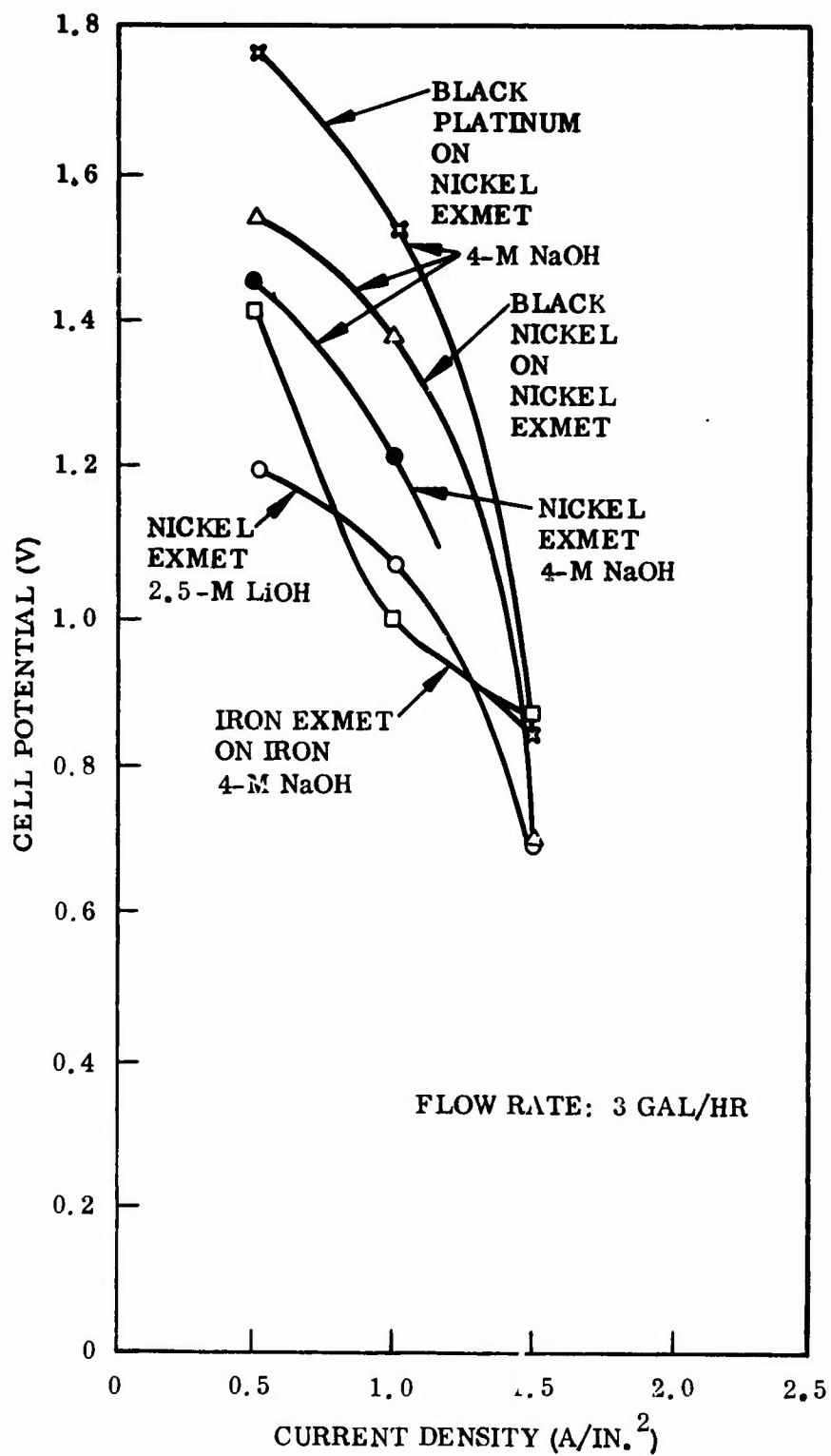


Figure 24. Effect of Cathode on Cell Potential at 32°C

Section 3

CONCLUSIONS AND RECOMMENDATIONS

Basic cell studies have shown that the spaced electrode cell can be operated with lithium hydroxide concentrations of 2.5 to 3.5 M at 10 to 30°C at current densities to 1.5 A/in.². Indications are that this is about half the power density that may be expected using optimized cell construction. Selected electrolytes may be used that allow 50- to 80-percent lithium utilization at potentials of over 1 V and at temperatures to 30°C. Still better efficiencies are possible with optimized compositions. Catalyzation decreases cathode polarization by 0.1 to 3 V and increases cell potential by the same value. This represents a 10- to 25-percent increase in power from the system.

The critical problems facing the system for the present application remain the reduction of parasitic losses at the anode to decrease heating, to increase the cell voltage under load, and to increase the power density. Parasitic anodic reaction may be reduced by the selection of an appropriate anode alloy. This selection is planned for this continuing effort. A tradeoff study of electrolyte concentration, current density and temperature, and lithium efficiency is also planned and should allow selection into the best operating conditions.

Increased voltage from the cell is possible using cathode catalysts, as was indicated by experiments during this work period. More comprehensive improvements could be expected using active cathodes because such use would increase the voltage by at least 1 V and reduce the volume of hydrogen that must be vented from the cell. A study of cells with active cathodes is recommended for future work. Power increase may be expected when the cell structure is changed from the open-spaced electrode structure to a flowthrough cathode structure with greatly reduced electrode spacing. This structure will be used for cell studies pointing toward the application of this device.

The lithium-water cell has been characterized during the present study, and marked improvements have been made in lithium utilization efficiency and in the cell potential by the use of catalyzed cathodes. If the planned and recommended studies and experiments are conducted during the next work period, the power available from the lithium-water cell should be increased sufficiently to meet the program goals.